UNIVERSITY OF ALBERTTA

Investigation of Viscoelastic Properties of Polymer Based Fluids as a Possible Mechanism of Internal Filter Cake Formation

©

By

Hassan Dehghanpour Hossein Abadi

A thesis
submitted to the Faculty of Graduate Studies and Research
in partial fulfillment of the requirements for the degree
of Master of Science in

Petroleum Engineering

Department of Civil and Environmental Engineering

Edmonton, Alberta
Fall, 2008

Library and
Archives Canada

Published Heritage
Branch

395 Wellington Street
Ottawa ON K1A 0N4
Canada

Bibliothèque et
Archives Canada

Direction du
Patrimoine de l'édition

395, rue Wellington
Ottawa ON K1A 0N4
Canada

Your file Votre référence
ISBN: 978-0-494-47201-9
Our file Notre référence
ISBN: 978-0-494-47201-9

NOTICE:
The author has granted a non-exclusive license allowing Library and Archives Canada to reproduce, publish, archive, preserve, conserve, communicate to the public by telecommunication or on the Internet, loan, distribute and sell theses worldwide, for commercial or non-commercial purposes, in microform, paper, electronic and/or any other formats.

The author retains copyright ownership and moral rights in this thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without the author's permission.

AVIS:
L'auteur a accordé une licence non exclusive permettant à la Bibliothèque et Archives Canada de reproduire, publier, archiver, sauvegarder, conserver, transmettre au public par télécommunication ou par l'Internet, prêter, distribuer et vendre des thèses partout dans le monde, à des fins commerciales ou autres, sur support microforme, papier, électronique et/ou autres formats.

L'auteur conserve la propriété du droit d'auteur et des droits moraux qui protège cette thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

In compliance with the Canadian Privacy Act some supporting forms may have been removed from this thesis.

While these forms may be included in the document page count, their removal does not represent any loss of content from the thesis.

Conformément à la loi canadienne sur la protection de la vie privée, quelques formulaires secondaires ont été enlevés de cette thèse.

Bien que ces formulaires aient inclus dans la pagination, il n'y aura aucun contenu manquant.

Canada

Abstract

This study aims at investigating the influence of elastic properties of aqueous polymer solutions on their flow behavior in porous media.

Different grades of Poly-Ethylene-Oxide (Polyox) were mixed to prepare polyox blends of approximately equal average molecular weight (M_w) and varying molecular weight distribution (MWD). A new mixing rule was suggested for prediction of the M_w of the polymer blends and the equivalent zero shear viscosity (μ_0) of their aqueous solutions. Proposed equation predicts more accurate values of μ_0 and M_w in comparison to the correlations available in the literature.

A series of core flow experiments was conducted by using aqueous solutions of two different blends of polyox with different MWD and similar M_w. The effect of MWD on both rheological properties and porous media pressure drop was investigated. Aqueous solutions of polyox blend with broader MWD and consequently more dominant elastic effects showed considerably higher pressure drop compared to that of narrow MWD blend.

The current theory of non-Newtonian fluid flow in porous media was revisited for possible improvement in pressure loss prediction by introducing the effect normal stress difference.

ACKNOWLEDGMENTS

I would like to express my sincere gratitude and appreciation to Dr. Ergun Kuru for his unconditional support, advice, encouragement and guidance throughout the course of this study.

Thanks are also sincerely expressed to Mr. Nathan Buzik for his invaluable technical advice in the design and construction of the experimental set up.

Finally, I would like to extend my deepest thank to my loving fiancé, mother and father for their patience and support during my studies.

This work has been supported by The Natural Sciences and Engineering Research Council of Canada (NSERC). Financial support from NSERC is greatly acknowledged.

TABLE OF CONTENTS

1 INTRODUCTION 1

1.1 OVERVIEW 1

1.2 STATEMENT OF THE PROBLEM 2

1.3 OBJECTIVES AND SCOPE OF THE RESEARCH 4

1.4 STRUCTURE OF THE THESIS 5

2 LITERATURE REVIEW 7

2.1 RHEOLOGICAL PROPERTIES OF AQUEOUS POLYMER SOLUTIONS 7

2.1.1 SHEAR VISCOSITY 7

2.1.2 NORMAL STRESS DIFFERENCE 8

2.1.3 EXTENSIONAL VISCOSITY 8

2.1.4 TROUTON RATIO 11

2.2 VISCOELASTIC BEHAVIOR OF SOME POLYMER SOLUTIONS 12

2.3 EFFECT OF AVERAGE MOLECULAR WEIGHT, MW, AND MOLECULAR WEIGHT DISTRIBUTION, MWD, ON RHEOLOGICAL BEHAVIOR OF POLYMERIC LIQUIDS 16

2.3.1 WEIGHT AVERAGE MOLECULAR WEIGHT 17

2.3.2 MOLECULAR WEIGHT DISTRIBUTION (MWD) 17

2.3.3 SHEAR VISCOSITY 18

2.3.4 RELAXATION TIME 19

2.3.5 UNIAXIAL ELONGATIONAL FLOW 20

2.4 QUALITATIVE ANALYSIS OF VISCOELASTIC FLOW THROUGH POROUS MEDIA 21

2.4.1 MOLECULAR CONFIGURATION OF POLYMER SOLUTIONS IN POROUS MEDIA 21

2.4.2 FLOW BEHAVIOR IN TORTUOUS CHANNELS 22

2.4.3 DEFORMATION OF VISCOELASTIC FLUIDS IN POROUS MEDIA 24

2.4.4 TRANSIENT NATURE OF VISCOELASIC FLOW IN POROUS MEDIA 25

2.4.5 CRITICAL FLOW RATE 28

2.4.6 POLYMER WALL INTERACTION 31

2.4.7 PRESSURE DUE TO FLOW OF VISCOELASTIC FLUIDS THROUGH COMPLEX GEOMETRIES 35

2.5 QUANTITATIVE ANALYSIS OF VISCOELASTIC FLOW THROUGH POROUS MEDIA 40

2.5.1 DEBORAH NUMBER 41

2.5.2 PRESSURE DROP-FLOW RATE RELATIONSHIP 42

3 EXPERIMENTAL PROGRAM 49

3.1 MATERIALS USED FOR THE PREPARATION OF POLYMER-BASED FLUIDS 49
3.2 DISSOLVING POLYOX IN WATER 49
3.3 PROCEDURE FOR PREPARATION POLYOX SOLUTIONS WITH SIMILAR SHEAR VISCOSITY AND DIFFERENT VISCOELASTIC PROPERTIES 50
3.4 RHEOLOGICAL TESTS 52
3.4.1 VISCOMETRY 54
3.4.2 OSCILLATION TEST 54
3.4.3 RELAXATION TEST 56
3.4.4 CREEP TEST 57
3.5 CORE FLOW EXPERIMENTS 59
3.5.1 EXPERIMENTAL SET-UP FOR CORE FLOW EXPERIMENTS 59
3.5.2 EXPERIMENTAL PROCEDURE 66

4 EXPERIMENTAL RESULTS AND DISCUSSION (RHEOLOGY) 69

4.1 RHEOLOGICAL CHARACTERIZATION OF MONODISPERSE POLYOX SOLUTIONS 69
4.1.1 Oscillation tests 71
4.2 RHEOLOGICAL CHARACTERIZATION OF POLYDISPERSE POLYOX SOLUTIONS 72
4.2.1 Mixing Rule 72
4.2.2 Polydispersity 76
4.2.3 Effect of MWD on shear viscosity of polyox blends 77
4.2.4 Effect of MWD on the viscoelastic behavior of polyox blends 78

5 EXPERIMENTAL RESULTS AND DISCUSSION (CORE FLOW EXPERIMENTS) 88

5.1 ABSOLUTE PERMEABILITY MEASUREMENT 88
5.2 EQUIVALENT SHEAR RATE 91
5.3 POLYOX SOLUTIONS 91
5.4 CORE FLOW EXPERIMENTS 92
5.4.1 High polymer concentration and high permeability experiments 92
5.4.2 Low polymer concentration and low permeability experiments 100
5.4.3 Permeability impairment 112
5.5 DISCUSSION 115

6 COMPARISON OF EXPERIMENTAL DATA AND THEORETICAL MODELS 119

6.1 MODELING OF RHEOLOGICAL PROPERTIES OF 3 WT % AQUEOUS POLYOX SOLUTIONS 119

6.2 CRITICAL FLOW RATE 125

6.3 COMPARISON OF EXPERIMENTAL PRESSURE DROP VALUES WITH THEORETICAL VALUES CALCULATED FROM DARCY EQUATION IN RADIAL SYSTEMS 131

6.3.1 High permeability-high polymer concentration case 131

6.3.2 Low permeability-low polymer concentration case 133

6.4 MODIFICATION OF DARCY EQUATION FOR ELASTIC EFFECTS OF POLYOX SOLUTIONS 138

7 CONCLUSIONS AND RECOMMENDATIONS 143

7.1 CONCLUSIONS 143

7.2 RECOMMENDATIONS: 146

REFERENCES 147

LIST OF TABLES

TABLE 2-1 FORMATION DAMAGE MEASURED AFTER THE FLOW OF POLYMER SOLUTIONS (KHAN ET AL. 2004). 34

TABLE 2-2 MEASURED AND CALCULATED PRESSURE LOSS VALUES (KHAN ET AL. 2004) 38

TABLE 3-1 POLYOX GRADES WITH DIFFERENT MOLECULAR WEIGHTS 49

TABLE 4-1 POLYDISPERSITY FACTOR AND COMPOSITION OF DIFFERENT POLYOX BLENDS 74

TABLE 4-2 MIXING RATIO AND APPROXIMATE POLYDISPERSITY VALUE OF TWO DIFFERENT POLYOX BLENDS 79

TABLE 4-3 ZERO-SHEAR RATE VISCOSITY AND DOMINANT RELAXATION TIME OF AQUEOUS SOLUTIONS OF SAMPLES 1 AND 2 (10 WT %). 81

TABLE 4-4 SUMMARY OF CREEP AND RECOVERY TEST RESULTS OF AQUEOUS SOLUTIONS OF SAMPLES 1AND 2 (10 WT %) 82

TABLE 4-5 LONGEST RELAXATION TIME AND THE RESULT OF OSCILLATION TEST AT FREQUENCY OF 1HZ FOR AQUEOUS SOLUTIONS OF SAMPLES 1 AND 2 (10 WT %) 86

TABLE 4-6 MEASURED VALUES OF PARAMETERS OF EQ. 4-8 FOR AQUEOUS SOLUTIONS OF SAMPLES 1-2 (10 WT %). 86

TABLE 5-1 PROPERTIES OF THE TWO DIFFERENT POROUS MEDIA USED IN CORE FLOW EXPERIMENTS 90

TABLE 5-2 TWO DIFFERENT SAMPLES OF POLYOX WITH SIMILAR AVERAGE MOLECULAR WEIGHT AND DIFFERENT POLYDISPERSITY VALUES 92

TABLE 6-1 POWER LAW PARAMETERS FOR SHEAR STRESS OF AQUEOUS SOLUTIONS OF SAMPLES 1 AND 2 (3 WT. %) 121

TABLE 6-2 POWER LAW PARAMETERS FOR FIRST NORMAL STRESS DIFFERENCE OF AQUEOUS SOLUTIONS OF SAMPLES 1 AND 2 (3 WT. %) 122

TABLE 6-3 RHEOLOGICAL PROPERTIES AND RELAXATION TIMES OF POLYOX SOLUTIONS AT EQUIVALENT SHEAR RATE WHERE DRAMATIC PRESSURE DROP IS OBSERVED 130

TABLE 6-4 CALCULATED VALUES OF DEBORAH NUMBER FOR POLYOX SOLUTIONS AT DIFFERENT PARTS OF THE RADIAL PACK 130

TABLE 6-5 MEASURED PRESSURE DROP AND PREDICTED VALUES FROM DARCY EQUATION FOR SAMPLE 2 (3 WT %) IN RADIAL PACKING (8.9 DARCY) 139

TABLE 6-6 MEASURED PRESSURE DROP AND PREDICTED VALUES FROM DARCY EQUATION FOR SAMPLE 2 (1 WT %) IN RADIAL PACKING (0.12 DARCY) 139

TABLE 6-7 COMPARISON BETWEEN AVERAGE VALUES OF ΔPMEASURED /ΔPDARCY AND N1/T FOR AQUEOUS SOLUTIONS OF SAMPLE 2 140

LIST OF FIGURES

FIG. 2-1 THE DIRECTION OF THE PRINCIPLE STRESSES IN UNIAXIAL ELONGATIONAL FLOW 9

FIG. 2-2 THE EXTENSIONAL VISCOSITY OF XANTHAN GUM SOLUTIONS, RELATIVE TO PREDICTIONS FROM BATCHELOR'S THEORY FOR SUSPENSIONS OF LONG RODS (SONG ET AL. 1996)... 11

FIG.2-3 SHEAR AND EXTENSIONAL VISCOSITY OF 1.5 LB/BBL XANTHAN GUM IN TAP WATER AT 75°C (NAVARETE ET AL. 2000)........ 12

FIG. 2-4 SHEAR RATE VS. TANGENTIAL AND NORMAL SHEAR STRESS FOR POLYMER SOLUTIONS (DATA TAKEN AT 75 F, 0.5°) (DAUBEN ET AL. 1966)........ 13

FIG. 2-5 VISCOMETRIC DATA FOR A 1500 PPM AQUEOUS SOLUTION OF XANTHAN GUM AND A 250 PPM AQUEOUS POLYACRYLAMIDE SOLUTION, 20°C (JONES ET AL. 1989)........ 14

FIG. 2-6 NORMALIZED VALUES OF TROUTON RATIO FOR DIFFERENT POLYMER SOLUTIONS (SONG ET AL. 1996)........ 15

FIG. 2-7 SHEAR VISCOSITY VERSUS SHEAR RATE FOR POLYSTYRENE BLENDS, 1.0 WT% IN DIETHYLPHTHALATE AT 25°C (PLOG ET AL. 2005)........ 19

FIG. 2-8 FLOW VISUALIZATION FOR A NEWTONIAN LIQUID, 1250 PPM AQUEOUS SOLUTION OF XANTHAN GUM AND A 250 PPM AQUEOUS SOLUTION OF POLYACRYLAMIDE, 20°C. R IS A REYNOLDS NUMBER (JONES ET AL. 1989)........ 22

FIG. 2-9 FLOW VISUALIZATION FOR A NEWTONIAN LIQUID, 1250 PPM AQUEOUS SOLUTION OF XANTHAN GUM AND A 250 PPM AQUEOUS SOLUTION OF POLYACRYLAMIDE, 20°C. R IS A REYNOLDS NUMBER (JONES ET AL. 1989)........ 23

FIG. 2-10 THE PERCENTAGE OF FLUID PASSING THROUGH NARROW CHANNELS AGAINST TOTAL FLOW RATE FOR A 1500 PPM AQUEOUS SOLUTION OF XANTHAN GUM AND A 250 PPM AQUEOUS SOLUTION OF POLYACRYLAMIDE, (RELATED TO FLOW VISUALIZATION SHOWN IN FIG. 2-9) 20°C (JONES ET AL. 1989)........ 24

FIG. 2-11 SCHEMATIC REPRESENTATION OF $(\Delta P, Q)$ BEHAVIOR IN THE CASE OF ELASTIC LIQUIDS (JONES ET AL. 1989)........ 28

FIG. 2-12 THE RATIO OF PRESSURE DROP TO FLOW RATE AGAINST FLOW RATE FOR A 1500 PPM AQUEOUS SOLUTION OF XANTHAN GUM AND A 250 PPM AQUEOUS SOLUTION OF POLYACRYLAMIDE (RELATED TO GEOMETRY SHOWN IN FIG. 2-9), 20° C (JONES ET AL. 1989)........ 30

FIG. 2-13 FLOW PERFORMANCE CURVES ILLUSTRATING EFFECT OF BEAD SIZE ON VISCOSITY RATIO (DAUBEN ET AL. 1966) 32

FIG. 2-14 FLOW PERFORMANCE CURVES ILLUSTRATING EFFECT OF MOLECULAR WEIGHT ON VISCOSITY RATIO (SOLUTION VISCOSITIES, 4 TO 5 CP) (DAUBEN ET AL. 1966) 33

FIG. 2-15 SCHEMATIC DIAGRAM OF THE MODEL GEOMETRIES (JONES ET AL. 1989) 36

FIG. 2-16 EXPERIMENTAL DATA FOR A 1600 PPM AQUEOUS SOLUTION OF XANTHAN GUM, 20°C (JONES ET AL. 1989) 36

FIG. 2-17 EXPERIMENTAL DATA FOR A 50 PPM AQUEOUS SOLUTION OF POLYACRYLAMIDE, 20° C (JONES ET AL. 1989) 37

FIG. 2-18 FLOW PERFORMANCE OF VARIOUS POLYMER SOLUTIONS IN POROUS MEDIA (DAUBEN ET AL. 1966) 40

FIG. 3-1 BOHLIN RHEOMETER USED FOR RHEOLOGICAL CHARACTERIZATION 53

FIG. 3-2 SAMPLE LOADING FOR CONE AND PLATE MEASURING GEOMETRY 53

FIG. 3-3 STRAIN RESPONSE OF A SOLID 55

FIG. 3-4 STRAIN RESPONSE OF A PURE LIQUID 55

FIG. 3-5 THREE DIFFERENT RESPONSE CURVES IN CREEP TEST 58

FIG. 3-6 CALCULATING JOC AND JOR USING CREEP AND RECOVERY CURVES 59

FIG. 3-7 SCHEMATIC OF EXPERIMENTAL SETUP OF CORE FLOW EXPERIMENT USING THE RADIAL CORE HOLDER 60

FIG. 3-8 SCHEMATIC OF EXPERIMENTAL SETUP OF CORE FLOW EXPERIMENT USING THE LINEAR CORE HOLDER 60

FIG. 3-9 POSITIVE DISPLACEMENT PUMP USED TO INJECT WATER AND POLYMER SOLUTIONS 61

FIG. 3-10 CALIBRATION CURVE FOR PUMP FLOW RATE 62

FIG. 3-11 RADIAL CELL WITH ONE INJECTOR AND TWO PRODUCER LINES 63

FIG. 3-12 CROSS SECTION OF THE CORE HOLDER SHOWING THE PRODUCING AND INJECTION LINES 64

FIG. 3-13 RADIAL CELL WITH INJECTION AND PRODUCTION LINES 65

FIG. 3-14 LINEAR CELL CONNECTED TO PRESSURE TRANSDUCER AND PRESSURE GAUGE 66

FIG. 4-1 SHEAR VISCOSITY VS. SHEAR RATE OF AQUEOUS SOLUTIONS OF DIFFERENT POLYOX GRADES (5 WT. %) 70
FIG. 4-2 NORMAL FORCE VS. SHEAR RATE OF AQUEOUS SOLUTIONS OF DIFFERENT POLYOX GRADES (5 WT. %) 70
FIG. 4-3 ELASTIC MODULUS-FREQUENCY PROFILE OF AQUEOUS SOLUTIONS OF 4 DIFFERENT POLYOX GRADES (6 WT. %) 71
FIG. 4-4 VISCOUS MODULUS-FREQUENCY PROFILE OF AQUEOUS SOLUTIONS OF 4 DIFFERENT POLYOX GRADES (6 WT. %) 72
FIG. 4-5 ZERO-SHEAR RATE VISCOSITY VERSUS MOLECULAR WEIGHT FOR 5 WT % AQUEOUS SOLUTION OF POLYOX 73
FIG. 4-6 COMPARISON OF MEASURED AND PREDICTED VALUES OF EQUIVALENT MOLECULAR WEIGHT OF POLYOX BLENDS (5 WT % AQUEOUS SOLUTION) 75
FIG. 4-7 COMPARISON OF MEASURED AND PREDICTED VALUES OF ZERO SHEAR VISCOSITY OF POLYOX BLENDS (5 WT % AQUEOUS SOLUTION) 76
FIG. 4-8 SHEAR VISCOSITY-SHEAR RATE PROFILE OF DIFFERENT POLYOX BLENDS (5 WT%) 77
FIG. 4-9 SHEAR VISCOSITY VS. SHEAR RATE OF AQUEOUS SOLUTIONS OF SAMPLES 1 AND 2 (10 WT %) 79
FIG. 4-10 STRESS RELAXATION PROFILE OF AQUEOUS SOLUTIONS OF SAMPLES 1-2 (10 WT %) ... 80
FIG. 4-11 RELAXATION SPECTRA OF AQUEOUS SOLUTIONS OF SAMPLES 1-2 (10 WT %) 81
FIG. 4-12 ELASTIC MODULUS VERSUS FREQUENCY OF AQUEOUS SOLUTIONS OF SAMPLES 1 AND 2 (10 WT %) 83
FIG. 4-13 VISCOUS MODULUS VERSUS FREQUENCY OF AQUEOUS SOLUTIONS OF SAMPLES 1 AND 2 (10 WT %) 84
FIG. 4-14 G'/G" VERSUS FREQUENCY OF AQUEOUS SOLUTIONS OF SAMPLES 1 AND 2 (10 WT %) 85
FIG. 5-1 PRESSURE DROP VS. FLOW RATE OF WATER IN THE LINEAR CORE (MEDIA 1) 89
FIG. 5-2 PRESSURE DROP VS. FLOW RATE OF WATER IN THE LINEAR CORE (MEDIA 2) 90
FIG. 5-3 SHEAR STRESS VS. SHEAR RATE OF AQUEOUS SOLUTIONS OF SAMPLES 1 AND 2 (3 WT%) 93

FIG. 5-4 SHEAR VISCOSITY VS. SHEAR RATE OF AQUEOUS SOLUTIONS OF SAMPLES 1 AND 2 (3 WT. %)........ 94

FIG. 5-5 FIRST NORMAL STRESS DIFFERENCE VS. SHEAR RATE OF AQUEOUS SOLUTIONS OF SAMPLES 1 AND 2 (3 WT. %)........ 95

FIG. 5-6 THE RATIO BETWEEN FIRST NORMAL STRESS DIFFERENCE AND SHEAR STRESS OF AQUEOUS SOLUTIONS OF SAMPLES 1 AND 2 (3 WT. %)........ 97

FIG. 5-7 RELAXATION TIME VS. SHEAR RATE FOR AQUEOUS SOLUTIONS OF SAMPLES 1 AND 2 (3 WT %)........ 98

FIG. 5-8 PRESSURE DROP-FLOW RATE FOR AQUEOUS SOLUTIONS OF SAMPLE 1 AND 2 (3 WT %).. 99

FIG. 5-9 SHEAR STRESS VERSUS SHEAR RATE FOR AQUEOUS SOLUTIONS OF SAMPLE 1 (1.25 WT %) AND SAMPLE 2 (1 WT %)........ 101

FIG. 5-10 SHEAR VISCOSITY VERSUS SHEAR RATE FOR AQUEOUS SOLUTIONS OF SAMPLE 1 (1.25 WT %) AND SAMPLE 2 (1 WT %)........ 102

FIG. 5-11 NORMAL FORCE VERSUS SHEAR RATE FOR AQUEOUS SOLUTIONS OF SAMPLE 1 (1.25 WT %) AND SAMPLE 2 (1 WT %)........ 103

FIG. 5-12 THE RATIO BETWEEN NORMAL FORCE AND SHEAR STRESS FOR AQUEOUS SOLUTIONS OF SAMPLE 1 (1.25 WT %) AND SAMPLE 2 (1 WT %)........ 104

FIG. 5-13 RELAXATION TIME VS. SHEAR RATE FOR AQUEOUS SOLUTIONS OF SAMPLE 1 (1.25 WT %) AND SAMPLE 2 (1 WT %)........ 105

FIG. 5-14 COMPARISON BETWEEN PRESSURE DROP OF SAMPLE 1 (1.25 WT %) AND SAMPLE 2 (1 WT %) DURING FLOW IN RADIAL POROUS MEDIA (0.12 DARCY)........ 106

FIG. 5-15 SHEAR STRESS VERSUS SHEAR RATE FOR AQUEOUS SOLUTIONS OF SAMPLE 1 (1.5 WT %) AND SAMPLE 2 (1 WT %)........ 107

FIG. 5-16 SHEAR VISCOSITY VERSUS SHEAR RATE FOR AQUEOUS SOLUTIONS OF SAMPLE 1 (1.5 WT %) AND SAMPLE 2 (1 WT %)........ 108

FIG. 5-17 NORMAL FORCE VERSUS SHEAR RATE FOR AQUEOUS SOLUTIONS OF SAMPLE 1 (1.5 WT %) AND SAMPLE 2 (1 WT %)........ 109

FIG. 5-18 THE RATIO BETWEEN NORMAL FORCE AND SHEAR STRESS FOR AQUEOUS SOLUTIONS OF SAMPLE 1 (1.5 WT %) AND SAMPLE 2 (1 WT %)........ 110

FIG. 5-19 RELAXATION TIME VS. SHEAR RATE BEHAVIOR FOR AQUEOUS SOLUTIONS OF SAMPLE 1 (1.5 WT %) AND SAMPLE 2 (1 WT %) 111

FIG. 5-20 COMPARISON BETWEEN PRESSURE DROP OF SAMPLE 1 (1.5 WT %) AND SAMPLE 2 (1 WT %) DURING FLOW IN RADIAL POROUS MEDIA (0.12 DARCY) 112

FIG. 5-21 COMPARISON OF PRESSURE DROP DUE TO WATER FLOW THROUGH POROUS MEDIA, IN CLEAN CORE AND AFTER INJECTION OF SAMPLES 1 AND 2 (RADIAL CELL, 0.12 DARCY) 114

FIG. 5-22 SCHEMATIC COMPARISON BETWEEN PRESSURE DROP-FLOW RATE PROFILE OF TWO DIFFERENT POLYMER SOLUTIONS WITH SIMILAR AVERAGE MOLECULAR WEIGHT AND DIFFERENT ELASTIC PROPERTIES (HIGH PERMEABILITY POROUS MEDIA) 118

FIG. 5-23 SCHEMATIC COMPARISON BETWEEN PRESSURE DROP-FLOW RATE PROFILE OF TWO DIFFERENT POLYMER SOLUTIONS WITH SIMILAR AVERAGE MOLECULAR WEIGHT AND DIFFERENT ELASTIC PROPERTIES (LOW PERMEABILITY POROUS MEDIA) 118

FIG. 6-1 FITTING POWER LAW MODEL TO EXPERIMENTAL VALUES OF SHEAR STRESS VS. SHEAR RATE (SAMPLE 1) 120

FIG. 6-2 FITTING POWER LAW MODEL TO EXPERIMENTAL VALUES OF SHEAR STRESS VS. SHEAR RATE (SAMPLE 2) 120

FIG. 6-3 FITTING POWER LAW MODEL TO EXPERIMENTAL VALUES OF NORMAL FORCE VS. SHEAR RATE 122

FIG. 6-4 COMPARISON OF MEASURED VALUES OF N1T AND PREDICTED VALUES (EQ. 6-6) FOR AQUEOUS SOLUTION OF SAMPLE 2 (3 WT %) 124

FIG. 6-5 TROUTON RATIO VERSUS DEBORAH NUMBER (CONSTANT STRAIN RATE) 126

FIG. 6-6 TROUTON RATIO VERSUS DEBORAH NUMBER AT DIFFERENT FLOW GEOMETRIES 128

FIG. 6-7 PRESSURE DROP-SHEAR RATE FOR AQUEOUS SOLUTIONS OF SAMPLE 1 (3 WT %) - COMPARISON OF EXPERIMENTAL RESULTS WITH PREDICTED VALUES FROM DARCY EQUATION 132

FIG. 6-8 PRESSURE DROP-SHEAR RATE FOR AQUEOUS SOLUTIONS OF SAMPLE 2 (3 WT %) AND COMPARISON OF EXPERIMENTAL RESULTS WITH THE VALUES PREDICTED FROM DARCY EQUATION 132

FIG. 6-9 COMPARISON OF MEASURED PRESSURE DROP FOR WATER FLOW IN RADIAL CELL AND THE ONES PREDICTED FROM DARCY EQUATION (PERMEABILITY: 0.12 DARCY).......... 133

FIG. 6-10 PRESSURE DROP VERSUS FLOW RATE OF SAMPLE 1 (1.25 WT %) IN RADIAL POROUS MEDIA (0.12 DARCY) AND COMPARISON WITH PREDICTED VALUES FROMDARCY EQUATION. 134

FIG. 6-11 COMPARISON OF MEASURED PRESSURE DROP VERSUS FLOW RATE OF SAMPLE 1 (1.5 WT %) IN RADIAL LOW PERMEABILITY PACK (0.12 DARCY) AND PREDICTED VALUES USING DARCY EQUATION 135

FIG. 6-12 COMPARISON BETWEEN RELAXATION TIME VS. SHEAR RATE BEHAVIOR OF AQUEOUS SOLUTIONS OF SAMPLE 1 136

FIG. 6-13 PRESSURE DROP VERSUS FLOW RATE OF SAMPLE 2 (1 WT %) IN RADIAL POROUS MEDIA (0.12 DARCY) AND COMPARISON WITH PREDICTED VALUES FROM DARCY EQUATION 138

FIG. 6-14 COMPARISON BETWEEN MEASURED PRESSURE DROP AND PREDICTED VALUES USING DARCY EQUATION AND SUGGESTED MODEL (EQ.6-20) FOR AQUEOUS SOLUTIONS OF SAMPLE 2 (3 WT %) 141

FIG. 6-15 COMPARISON BETWEEN MEASURED PRESSURE DROP AND PREDICTED VALUES USING DARCY EQUATION AND SUGGESTED MODEL (EQ.6-20) FOR AQUEOUS SOLUTIONS OF SAMPLE 2 (1 WT %) 142

LIST OF NOMENCLATURES

Symbol	
A	Cross section area
C_i	Empirical constant
C_N	Empirical constant
D	Diameter
D_0	Initial diameter of the filament
D_P	Particle diameter
De	Deborah number
DRI	Differential refractometer
El	Ellis number
EOR	Enhanced oil recovery
f	Friction factor
F	Empirical constant
G	Mass flow rate (Eq. 2.24)
G	Elastic modulus (Eq. 2.17)
G(t)	Relaxation modulus
G'	Elastic modulus
G''	Viscous modulus
G^*	Complex modulus
H(τ)	Relaxation spectra
J_0	Recoverable compliance
Joc	Recoverable compliance (Creep test)
Jor	Recoverable compliance (creep-recovery test)
k	Permeability
k_f	After-flush permeability
K	Constant parameter
L	Length
m	Power-law index
M_c	Critical molecular weight

M_i	Power-law index for normal stress or extensional viscosity
M_n	Numbered average molecular weight
M_w	Average molecular weight
$M_{W,B}$	Weighted average molecular weight of the blend
$M_{w,i}$	Average molecular weight
MALLS	Multi angle laser light scattering
MWD	Molecular weight distribution
$\bar{n}$	Average porous medium power law exponent
n	Power-law exponent
n_i	Power-law exponent for normal stress or extensional viscosity
N_1	First normal stress difference
N_2	Second normal stress difference
P	Pressure
PHPA	Partially hydrolyzed polyacrylamide
Q	Flow rate
R	Radius
r	Aspect ratio of polymer molecules
r_{max}	Maximum radius
r_{min}	Minimum radius
Re	Reynolds number
SEC	Size-exclusion-chromatography
t	Time
Tr	Trouton ratio
t_c	Charactristic time
v	Fluid velocity
ω_i	Mass fraction
WSR	Water soluble resin
XG	Xanthan gum

Greek Symbol

α	Power-law exponent for shear viscosity (Eq. 2.37)
β	Empirical constant
$\dot{\gamma}$	Shear rate
γ	Strain
Δ	Difference
δ	Phase angle
$\dot{\varepsilon}$	Strain rate
θ	Relaxation time
θ_0	Longest relaxation time
μ_o	Zero-shear rate viscosity
μ	Shear viscosity
μ_e	Extensional viscosity
ρ	Density
σ	Surface tension
τ	Shear stress
τ_{11}	First principle stress
τ_{22}	Second principle stress
τ_{33}	Third principle stress
τ_{ik}	Stress in the direction of i inside the plan perpendicular to k axis
$\tau_{1/2}$	Shear stress at shear rate where shear viscosity is half of zero shear Viscosity
τ_{RH}	Shear stress at hydraulic radius
φ	Porosity
ψ	Empirical constant

Sub-scripts

1	Sample 1
2	Sample 2
B	Polyox blend
B	Broad molecular weight distribution (Fig. 5.23)
Cr	Critical
I	Inside diameter
N	Narrow molecular weight distribution (Fig. 5.23)
m	Medium diameter
o	Outside diameter

CHAPTER 1

INTRODUCTION

1.1 Overview

Viscoelastic behavior of polymer solutions in porous media is increasingly of pivotal importance to many petroleum engineering applications such as acidizing, fracturing, secondary recovery methods (i.e., water and gas flooding, steam injection, in situ combustion), gas cycling, etc. Polymer solutions of different concentrations and rheological properties are increasingly and widely used in petroleum engineering applications.

During drilling it is a common practice to maintain a positive pressure difference between the drilling fluid and the formation. Overbalanced drilling causes the mud particles and mud filtrate to invade the formation. Thus, the permeability of near wellbore formation is generally altered and this alteration induces strong detrimental effects on well productivity.

Any type of a process, which results in a reduction of the flow capacity of an oil, water or gas bearing formation, is defined as formation damage. Different mechanisms have been known for formation damage including sand and fines migration, clay swelling, organic precipitation and scale.

Success of the horizontal wells is very often impaired with productivity reduction due to formation damage. The economic impact of poor productivity of open-hole horizontal wells has pushed research institutions towards spending significant research efforts in recent years to investigate drilling induced formation damage. Despite all the efforts, questions still remain regarding the formulation of optimum fluid composition to minimize, if not eliminate, productivity impairment due to formation damage.

Several industrial ideas have been proposed for designing drilling fluids with minimum invasion into the reservoir rock. Since blocking agents added to drilling fluid block pores near the well bore, acid treatment is usually required for their removal. In polymer flooding, small concentrations of high molecular weight polymers are added to the displacement fluid. Large polymer molecules increase the viscosity and decrease the mobility of the solvent. This decrease in fluid mobility improves the volumetric sweep efficiency of the water flood. A thicker displacement fluid helps to prevent the phenomenon of viscous fingering, which has an adverse effect on oil extraction. It is clear that, in any comprehensive study of enhanced oil recovery, rheology must play a role (Jones et al. (1989)).

Even after decades of research, the mechanism of polymer flow in porous media remains vaguely understood.

1.2 Statement of the Problem

As the bit penetrates the reservoir rock, the continuous phase of drilling fluid invades the formation due to the positive pressure differential between the well and reservoir rock. Presence of mud filtrate in the reservoir zone significantly decreases relative permeability of oil and gas that consequently results in productivity reduction.

Drilling fluid filtration into the reservoir rock during drilling, completion and stimulation may also result in: borehole instability, excessive torque and drag, pipe stuck due to differential pressure and formation damage (Cobianco et al. (1999)).

Permeability impairment is more pronounced in case of horizontal wells where drilling/completion fluids remain in contact with pay zone for longer time. Production results from many horizontal wells have been disappointing. It is believed that when this has occurred in situations where reservoir quality is good, near wellbore formation damage effects of drilling, well completion and even stimulation (hydraulic fracturing) fluids have been the major contributor to the poor production performance (Bennion et al. (1996)).

Generally, filtration loss is controlled by increasing the viscosity of drilling fluid by viscosifier additives (Navarete et al. (1995); Parlar et al. (1995)). Filter cake developed by bridging agents in drilling fluid reduces the filtration loss (Penny et al. (1989). However, such agents often require acid treatment for their removal.

Polymer based drilling fluids may be designed in such a way that they would generate extremely high pressure drop when flowing through a porous media without generating extra losses while flowing in the well (Martins et al. (2005)). Non-invasive solids free drilling fluid is beneficial as acid treatment is not required for removal of blocking agents.

The use of Darcy's law for modeling polymer flow in porous media has serious flaws because: (1) viscosity of polymer solutions depends on shear rate, (2) length of polymer molecules is comparable to the pore throat length, a fact that enhances certain elastic phenomena, and (3) adsorption and entrapment of polymer molecules in porous media may result in permeability impairment (Garrouch et al. (2006)).

Polymer based fluids exhibit significant elongational components as they flow through porous media due to the rapid changes in the cross-sectional area of the pore space in the flow direction. It is found that, above a critical set of conditions, a significant increase in the flow resistance of polymer solutions in a porous medium is observed (James et al (1975); Marshall et al (1967); Ghoniem (1985)). Unexpected high flow resistance of polymer solutions has been observed in experiments performed with polyethylene oxide and polyacrylamide solutions (Dauben et al. (1967), Marshal et al. (1967), James et al. (1975)).

Viscoelastic properties of polymer solutions such as extensional viscosity, first normal stress difference and relaxation time influences flow resistance in porous media. Extensional deformation of fluid elements in porous media dominates the elastic effects. Saasen et al. (1990) showed the influence of G' and G'' on the flow of polymer based fluids through porous media. Relaxation time of polymer solutions also significantly influences the flow behavior in porous media (Gupta et al. 1985; Sadowski et al. 1965).

It has been widely accepted in polymer science that the size and structure of polymer molecules significantly influence their rheological properties (Bird et al. 1977). Zero-shear rate viscosity (μ_0) and relaxation time of aqueous polymer solutions strongly depend on the average molecular weight (Ferry 1980). As long as the average molecular weight is constant, however, molar mass distribution weakly influences μ_0.

MWD strongly influences steady state rheological properties of polymer solutions. By changing the molar mass distribution of polymer mixtures while keeping the average molecular weight constant, the pressure losses due the flow of aqueous polymer solutions through porous media may be controlled. This type of flow has a very practical appeal in many petroleum engineering applications, as controlling the damage due to fluid invasion into the reservoir rock has a significant impact on the rate of oil and gas production rates.

The aim of this research is to investigate the influence of elastic properties of polymer solutions on flow resistance in porous media. Rheological properties of polymer solutions responsible for extra flow resistance in porous media may be optimized by controlling MWD at constant average molecular weight. This would facilitate formulation of optimum drilling, well completion and fracturing fluid compositions with minimum formation damage effect.

1.3 Objectives and scope of the research

The primary objective of this research study is to investigate the influence of elastic properties of polymer solutions on flow resistance in porous media. This was done by injecting aqueous solutions of Polyethylene oxide with varying molecular weight distribution and similar average molecular weight into the porous media.

The second objective of this research is to modify Darcy equation for predicting pressure drop of polymer solutions in porous media by considering both viscous and elastic properties of the fluid.

To achieve these research objectives the following tasks have been completed and are described in this thesis:

1) Literature survey and discussion
2) Rheological characterization of aqueous solutions of different grades of polyox with varying average molecular weight at different concentrations.
3) Prepare aqueous solutions of polyox blends with similar average molecular weight (i.e., similar shear viscosity) and different molecular weight distribution.
4) Viscoelastic characterization of polyox blends with similar shear viscosity and different molecular weight distribution by conducting rheological tests including viscometry, relaxation and oscillation tests.
5) Core flow experiments in radial cell with varying permeabilities using aqueous solutions of two different polyox blends with similar shear viscosity and different molecular weight distribution.
6) Modification of Darcy equation to account for elastic properties of polyox solutions.

1.4 Structure of the thesis

Chapter 1 gives an overview of the research work. It outlines the background and statement of the research problems, the objectives and the scope of the work.

Chapter 2 gives a comprehensive literature review and discussion of the subject area.

Chapter 3 describes the methodology followed throughout this study. A detailed description of rheometer and different rheological tests used for viscoelastic characterization of polymer solutions, detailed description of experimental set-up and procedure for core flow experiments.

Chapter 4 presents the results of rheology measurements of aqueous solutions of different grades of Polyox and blended polyox samples.

Chapter 5 provides the result of core flow experiment using aqueous solution of different blends of polyox.

Chapter 6 provides the details of proposed model for predicting pressure drop due to viscoelastic effects in porous media.

Chapter 7 presents the conclusions of the research as well as recommendations for future works.

CHAPTER 2

LITERATURE REVIEW

2.1 Rheological properties of aqueous polymer solutions

2.1.1 Shear viscosity

Shear viscosity is physically a measure of fluid resistance against shear forces during flow that is defined as the ratio between shear stress and shear rate. Basically viscosity of a fluid is a function of temperature and pressure. Shear viscosity of Newtonian fluids is constant at specific thermodynamic conditions that is defined by:

$$\tau = \dot{\gamma}\, \mu \tag{2-1}$$

Where, μ is Newtonian viscosity that is a function of temperature and pressure of fluid and independent of shear rate. τ and $\dot{\gamma}$ are shear stress and shear rate respectively.

Shear viscosity of a non-Newtonian fluid is strongly dependent on deformation rate. Basically two different rheological behaviors are considered for non-Newtonian fluids:

- Shear thinning behavior
- Shear thickening behavior

Viscosity of most of polymer solutions linearly decreases with shear rate in logarithmic coordinate. Power law relationship is commonly used to model non-Newtonian viscosity of polymer solutions.

$$\tau(\dot{\gamma}) = m\, \dot{\gamma}^{n} \tag{2-2}$$

$$\mu(\dot{\gamma}) = m\, \dot{\gamma}^{n-1} \tag{2-3}$$

m and n are power law constants that could be obtained by fitting a straight line to the experimental data in log-log scale.

2.1.2 Normal stress difference

Normal stress difference is an important material function of polymer solutions indicating the degree of elasticity of large polymer molecules. Normal stress values could be interpreted as an indication of the ability of polymer molecules to deform under applied stresses. First and second normal stress difference are defined by (Bird et al. 1977):

$$N_1(\dot{\gamma}) = \tau_{11} - \tau_{22} \tag{2-4}$$

$$N_2(\dot{\gamma}) = \tau_{22} - \tau_{33} \tag{2-5}$$

In this expression τ_{11} is normal stress in direction of flow and τ_{22} and τ_{33} are induced normal stress perpendicular to the flow direction. $N_1 and\ N_2$ are almost zero in case of a Newtonian fluid. However normal forces induced during flow of a non-Newtonian fluid (e.g. polymer solutions) could be significantly high. The value of N_2 is approximately 1/10 of N_1.

2.1.3 Extensional viscosity

Extensional viscosity is a measure of fluid resistance against tensile stress. In a uniaxial flow in a given direction, x, the following velocity and stress fields could be considered:

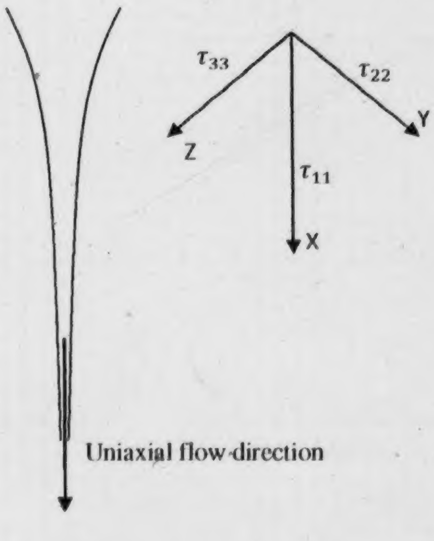

Fig. 2-1 The direction of the principle stresses in uniaxial elongational flow

$$v_x = \dot{\varepsilon}\, x \tag{2-6}$$

$$v_y = -\dot{\varepsilon}\, y/2 \tag{2-7}$$

$$\tau_{11} - \tau_{22} = \tau_{11} - \tau_{33} = \dot{\varepsilon}\, \mu_e(\dot{\varepsilon}) \tag{2-8}$$

$$\tau_{ik} = 0, i \neq k \tag{2-9}$$

Where, $\dot{\varepsilon}$ and $\mu_e(\dot{\varepsilon})$ are the strain rate and extensional viscosity respectively. v_x and v_y are fluid velocity in *x* and *y* direction. τ_{ik} is stress in the direction of i direction inside the plan perpendicular to k axis. Considering the definition of normal force, extensional viscosity for uniaxial elongational flow is given by:

$$\mu_e(\dot{\varepsilon}) = \frac{\tau_{11} - \tau_{22}}{\dot{\varepsilon}} = \frac{N_1}{\dot{\varepsilon}} \tag{2-10}$$

Therefore, highly elastic fluids (e.g. PHPA solutions) showing significant normal stress difference, are anticipated to have high extensional viscosity according to Eq. 2-10. For a Newtonian fluid it is shown in the literature (Jones et al. 1987) that the extensional viscosity is three times of the shear viscosity. Extensional viscosity of a viscoelastic fluid may be several orders of magnitude higher than their shear viscosity. Extensional viscosity, μ_e, strongly influences flow performance of polymer solutions in flow systems which give rise to elongational deformation such as porous media.

Cathey et al. (1988) gave the following equation to predict the extensional viscosity of a solution.

$$\mu_e = 3\mu_s + \frac{1}{3}\frac{\mu_s \vartheta r^2}{\ln(\pi/\vartheta)}$$

2-11

The first term is related to the extensional viscosity of solvent that is three times of its shear viscosity. The second term accounts for the effect of polymer molecules where ϑ the volume fraction of solids in solution and r is the aspect ratio of polymer molecules. Song et al. (1996) compared the predicted values of extensional viscosity of XG using Eq. **2-11** to experimental data (See Fig. 2-2).

According to the data shown in Fig. 2-2, the ratio of measured to predicted extensional viscosity values values scatter about 1. However, for viscous solutions this ratio is approximately equal to 1.3 (Song et al. 1996).

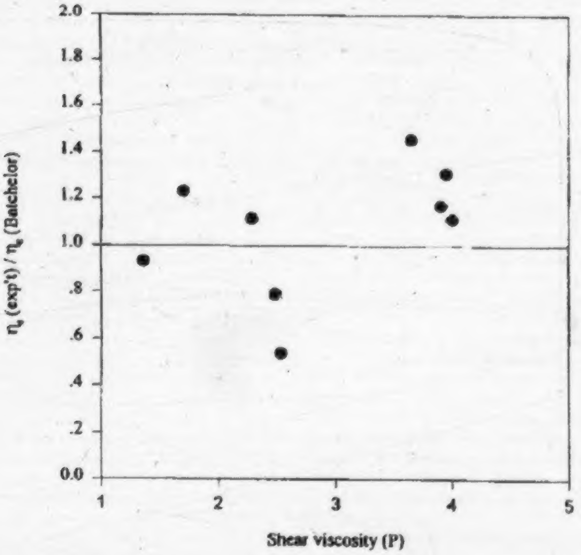

Fig. 2-2 The extensional viscosity of xanthan gum solutions, relative to predictions from Batchelor's theory for suspensions of long rods (Song et al. 1996).

2.1.4 Trouton ratio

Trouton ratio is an important rheological parameter in studying the viscoelastic characteristics of non-Newtonian fluids. This quantity represents the ratio of extensional viscosity to shear viscosity.

$$Tr = \frac{\mu_e(\dot{\varepsilon})}{\mu\,(\dot{\gamma})}$$

2-12

As the definition of shear rate and strain rate is different from each other, Jones et al. (1987) suggested the following expression for Tr.

$$Tr = \mu_e(\dot{\varepsilon})/\mu(\sqrt{3}\dot{\varepsilon})$$

2-13

They showed that Trouton number is 3 for Newtonian fluids with insignificant elastic properties. They also concluded that high values of Tr is related to viscoelasticity of the fluid.

Fig.2-3 shows the Trouton ratio of xanthan gum solution as a function of shear rate. Both shear viscosity and extensional viscosity of XG solution decreases with increasing the shear rate. Shear viscosity of XG decreases faster than extensional viscosity. Therefore, Trouton value and consequently elastic effects of XG solution increases with increasing shear rate.

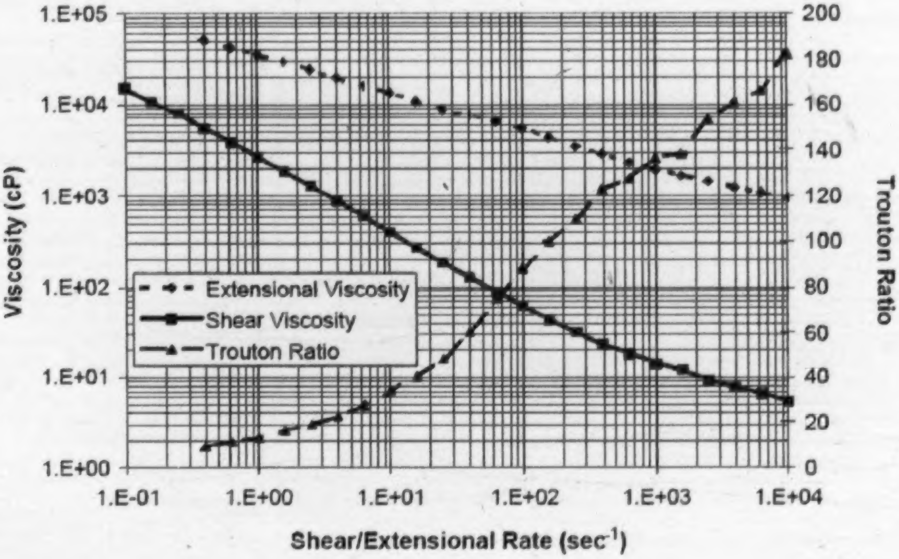

Fig.2-3 Shear and extensional viscosity of 1.5 lb/bbl Xanthan gum in tap water at 75°C (Navarete et al. 2000)

2.2 Viscoelastic behavior of some polymer solutions

Dauben et al. (1966) measured normal and tangential forces of aqueous solutions of three different grades of polyox (see Fig. 2-4).

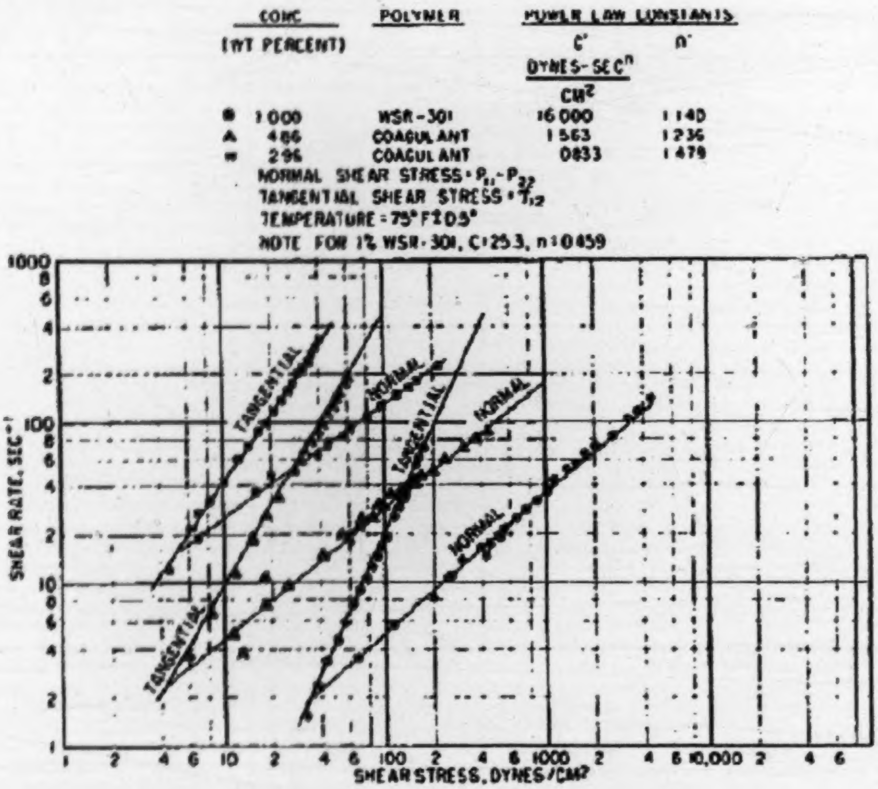

Fig. 2-4 Shear rate vs. tangential and normal shear stress for polymer solutions (Data taken at 75 F, 0.5°) (Dauben et al. 1966)

According to the presented data the following results could be obtained:

- Both normal and tangential stresses increase considerably with increasing the shear rate.
- Both tangential and normal curves tend to be linear in a log-log scale. It means that power law relationship may be used to model both normal stress and shear stress values as a function of shear rate.
- The value of normal stress and also its rate of increase are higher than shear stress.

Jones et al. (1989) measured viscosity and normal stress difference of aqueous solutions of polyacrylamide and xanthan gum at different shear rates (see Fig. 2-5).

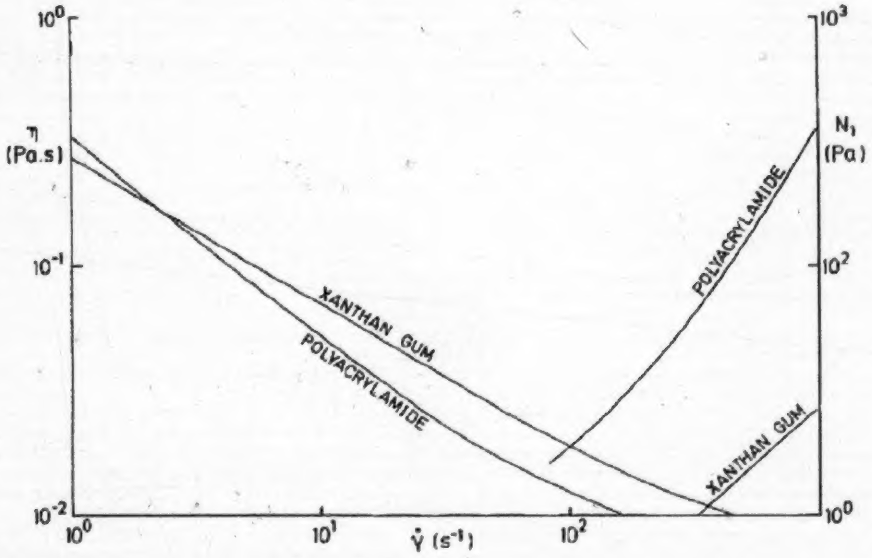

Fig. 2-5 Viscometric data for a 1500 ppm aqueous solution of xanthan gum and a 250 ppm aqueous polyacrylamide solution, 20°C (Jones et al. 1989)

Fig. 2-5 highlights the shear thinning behavior of the two solutions. Shear viscosity of xhanthan gum is relatively higher than that of polyacrylamide solution. While, the value of N_1 is considerably higher in case of polyacrylamide compared with xanthan gum. Therefore, flow behavior of polyacrylamide is controlled by both viscous and elastic forces, while, flow performance of XG is mainly influenced by viscous effects. High values of normal forces in case of polyacrylamide are mainly due to its highly flexible molecules.

Song et al. (1996) measured the extensional viscosity of some polymer solutions that is shown in Fig. 2-6. Normalized values of Trouton ratio are plotted versus extensional rate because solvents used in each solution had different Trouton values.

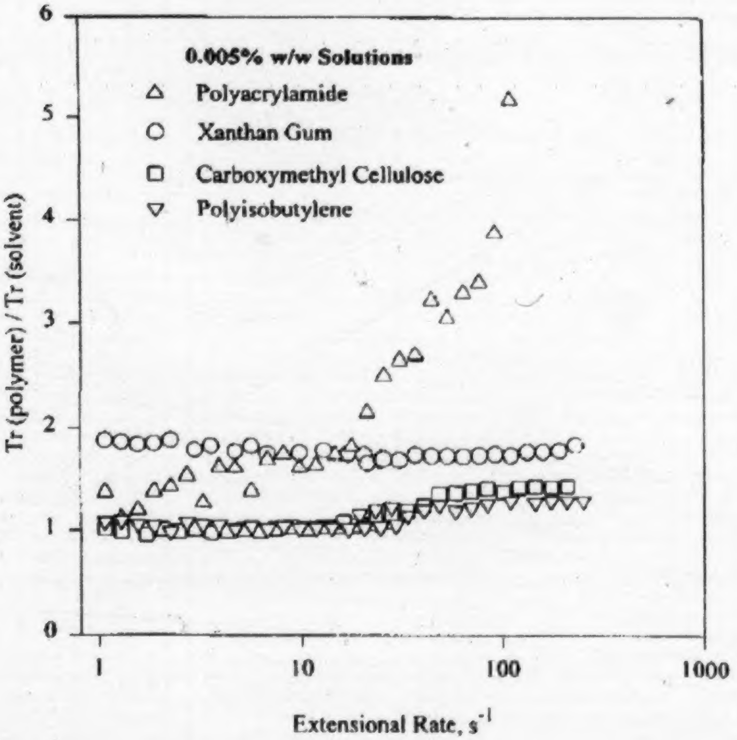

Fig. 2-6 Normalized values of Trouton ratio for different polymer solutions (Song et al. 1996)

Trouton value of all solutions except polyacrylamide tends to remain constant. Due to moderate elastic properties of XG, the ratio between the Trouton value of solution and solvent (that is a Newtonian fluid) is more than one. Although, Trouton ratio of polyacrylamide solution is relatively lower than XG solution at low shear rates, it starts increasing dramatically at a certain shear rate. It appears that after a critical flow rate high values of normal stress difference significantly influence the extensional viscosity of polyacrylamide (see Fig. 2-5 and Fig. 2-6). Therefore, identification of such critical deformation rates is essential for proper prediction of flow performance of viscoelastic fluids. Jones et al. (1989) suggested that there is a "critical strain rate region" where elastic forces dominantly influence the flow behavior and extensional viscosity plays an important role on behavior of fluid in porous media.

Chauveteau et al. (1984) showed that XG solution presents shear thinning characteristics in both shear and extensional flow, while PHPA solutions present dilatant behavior to extension and pseudoplastic behavior to shear.

2.3 Effect of average molecular weight, M_w, and molecular weight distribution, MWD, on rheological behavior of polymeric liquids

It has been widely accepted in polymer science that the size and structure of polymer molecules significantly influence their rheological properties (Bird et al. 1977). Above a critical molecular weight as a property of each polymer, entanglement of polymer molecules has a crucial influence on viscoelastic properties of the solution. Zero-shear rate viscosity, μ_0, and relaxation time of polymeric liquids are strongly related to the average molecular weight (Ferry 1980). Molar mass distribution however, while the average molecular weight is constant, weakly influences μ_0.

MWD strongly influence steady state rheological properties. It has been shown in literature that longest relaxation time as an important parameter of Non-Newtonian flow is influenced by MWD (Kulicke 1986; Liu et al. 1998; Shaw et al. 1994). Plog et al. (2005) showed the effect of molar mass distribution on uniaxial flow of two polymeric systems in capillary break up experiment. Furthermore, viscoelastic response of polymer melts in rheological tests such as relaxation test has been widely used for determination of MWD (McGrory and Tuminello 1990; Wasserman 1995; Leonardi et al. 2002).

The strain applied in simple shear flow is high enough to destroy the elastic structure of a polymeric system. However, at low strain flow systems the elastic component may strongly influence flow behavior of viscoelastic materials. Saasen et al. (1990) showed the influence of elastic and viscous modulus (G' and G") on flow through porous media. Relaxation time of polymer solutions also significantly influence flow behavior in porous media (Gupta et al. 1985; Sadowski et al. 1965). Therefore, by controlling the molar mass distribution of polymer mixtures at constant average molecular weight (and consequently their shear viscosity) viscoelastic parameters such as longest relaxation time, viscous and elastic modulus, influencing the flow behavior in special flow geometries such as elongational flow through porous media, may be controlled. In other words, polymer blends may be produced with similar viscous flow behavior while they have different performance in flow geometries promoting viscoelastic effects such as porous media.

2.3.1 Weight average molecular weight

Zero shear viscosity, μ_0, as an intrinsic property of polymer solutions at a certain concentration, is linked to average molecular weight of polymer. Eq. 2-14 represents zero shear viscosity as a function of average molecular weight (Ferry 1980).

$$\mu_0 = KM_w^a \tag{2-14}$$

K is a constant that depends on the type of polymer and the temperature. The weight average molecular weight of a mixture of monodisperse polymers of the same type, $M_{W,B}$,is given by (Zang 1987):

$$M_{W,B} = \sum_{i=1}^{n} \omega_i M_{w,i} \tag{2-15}$$

Where, ω_i is the mass fraction of monodisperse polymer with the molecular weight of $M_{w,i}$. Zero shear viscosity – molecular weight profile of linear polymer systems shows two different regions (Graessley, 1974). Above a critical molecular weight (M_c) as a property of each polymer, entanglements of polymer molecules have a crucial influence on their viscoelastic properties.

According to 2-14 blended polymer samples with similar weight-average molecular weight are expected to show similar shear behavior.

2.3.2 Molecular weight distribution (MWD)

The effect of MWD on rheological properties of polymers is explained in literature by considering the polydispersity values. Polydispersity value is defined as the ratio of M_w to

M_n. Where M_w is weight-average molecular weight and M_n is number-average molecular weight defined by (Zang 1987):

$$\frac{1}{M_{n,B}} = \sum_{i=1}^{n} \frac{\omega_i}{M_{n,i}} \qquad 2\text{-}16$$

The combination of the following techniques are used to measure the value of polydispersity ($\frac{M_w}{M_n}$):

- SEC (Size-exclusion-chromatography)
- MALLS (multi angle laser light scattering)
- DRI (differential refractometer)

2.3.3 Shear viscosity

Molar mass distribution, while the average molecular weight is constant, weakly influence zero–shear rate viscosity (Ressia et al. 2000). Fig. 2-7 shows shear viscosity of polystyrene blends with varying MWD as a function of shear rate. This figure highlights that the flow performance of different blends in shear flow is approximately the same. Therefore, shear flow behavior of different blends of polystyrene with the same molecular weight may not be influenced by molar mass distribution.

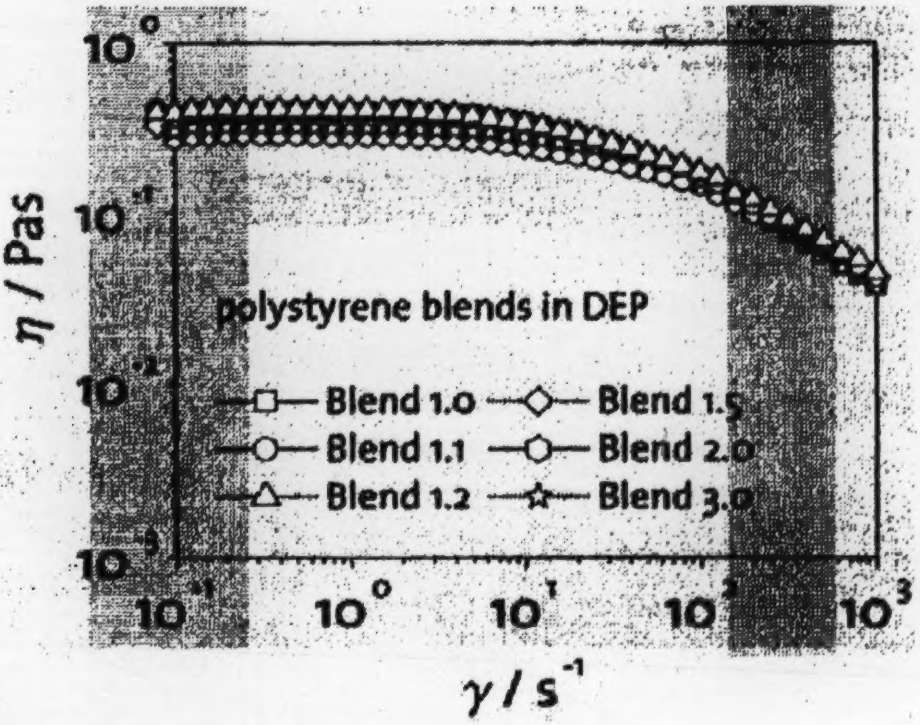

Fig. 2-7 Shear viscosity versus shear rate for polystyrene blends, 1.0 wt% in diethylphthalate at 25°C (Plog et al. 2005)

2.3.4 Relaxation time

It has been shown in literature that longest relaxation time as an important parameter of non-Newtonian flow is influenced by MWD (Kulicke 1986; Liu et al. 1998; Shaw et al. 1994). Viscoelastic response of polymer melts in rheological tests such as relaxation test has been widely used for determination of molecular weight distribution (McGrory et al. 1990; Wasserman 1995; Leonardi et al. 2002). (Plog et al. 2005) tried to correlate the relaxation times of blended polymers (determined via capillary breakup extensional rheometry) with the different moments of the MWD. In contrast to shear flow relaxation time, the values of relaxation time calculated using capillary breakup data are significantly influenced by MWD (Plog et al. 2005).

2.3.5 Uniaxial elongational flow

Elongational flow has been known as a new method to investigate the effect of MWD on rheological properties of polymer solutions. It has been observed that different polymer blends of the same average molecular weight and similar shear flow behavior present different performance in flow systems such as:

- Droplet breakup
- Filament formation
- Nozzle extrusion

(Plog et al. 2005) characterized commercially available blended methyl-hydroxy-ethyl and also blended polystyrene standards with similar M_w and varying MWD in capillary break up experiment. They observed different rate of filament diameter decrease for different polymer blends. The rate of filament diameter decrease of a viscoelastic fluid is controlled by the following equation (Clasen et al. 2006):

$$D = \left(\frac{G\,D_0}{4\,\sigma}\right)^{1/3} D_0 e^{\frac{-t}{3\theta_0}} \tag{2-17}$$

Where, D_0 and σ are initial filament diameter and surface tension of the investigated fluid. According to Eq. 2-16 the thinning behavior of filament is influenced by longest relaxation time (θ_0) and elastic modulus (G). Therefore, considering the different thinning behavior of blended samples, the effect of MWD on G and/or θ_0 may be concluded. Regarding the definition of extensional viscosity and different forces applied on thinning filament, the extensional viscosity is given by Eq. 2-18 (Plog et al. 2005).

$$\mu_e \approx \frac{\sigma}{-\frac{dD_{mid}}{dt}} \tag{2-18}$$

Therefore, elongational flow behavior (i.e., extensional viscosity) of different polymer blends with similar shear flow behavior could be different. It means that MWD and $\frac{M_w}{M_n}$ of polymeric systems influence their flow behavior in elongational flow systems. Higher ratio of heavy molecules in wider MWD samples may result in longer relaxation time and higher resistance against extensional flow.

2.4 Qualitative analysis of viscoelastic flow through porous media

Large polymer molecules with coiling configuration exhibit significant elastic effects during flow through porous media. Tortuous nature of porous media enhances viscoelastic effects due to multi-component deformation of fluid in tortuous channels of porous media. Relative magnitude of fluid relaxation time and its deformation rate during flow in packed beds strongly influences viscoelastic flow behavior. Interaction between polymer molecules and porous media could considerably reduce the effective permeability of flow system. Therefore, combined effects of fluid viscoelastic properties, flow geometry complexity as well as polymer-wall interaction results in extra pressure drop that is more pronounced at flow rates higher than a critical value.

2.4.1 Molecular configuration of polymer solutions in porous media

Polymer molecules can easily be dissolved in water by means of hydrogen bonding. However, some of their structural identity would be retained in aqueous solution. Non-ionic polymers with random coiling configuration (e.g., polyethylene oxide) have the ability to hold a large volume of solvent within their coil in a manner similar to that of a sponge (Dauben et al. 1966). Such random coils under applied stresses easily deform. Therefore, spherical orientation of such molecular structures change into elongated ellipsoids after deformation. Furthermore the coils are extensively entangled with each other and must drag along other coils in order to flow in a complex geometry such as porous media. Stressed polymer macromolecules generate significant elastic energy that could be quantified by normal stress value (Dauben et al. 1966).

2.4.2 Flow behavior in tortuous channels

Jones et al. (1989) conducted some visualization experiments to investigate the flow behavior of different fluid types in some asymmetric geometries. Fig. 2-8 compares the flow performance of three different types of fluids while flowing through a tortuous geometry.

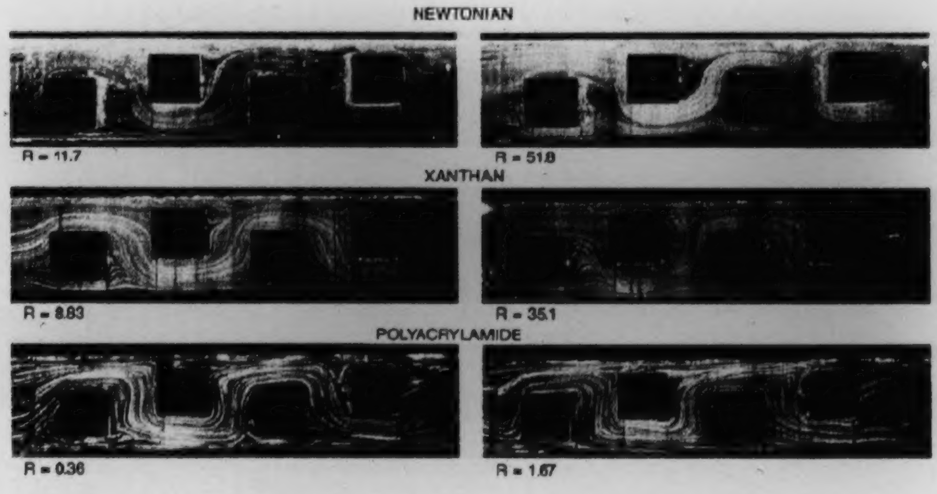

Fig. 2-8 Flow visualization for a Newtonian liquid, 1250 ppm aqueous solution of xanthan gum and a 250 ppm aqueous solution of polyacrylamide, 20°C. R is a Reynolds number (Jones et al. 1989)

According to pictures shown in Fig. 2-8, at high Reynolds numbers a significant part of both Newtonian fluid and xanthan gum solutions passes through the narrow channels. But polyacrylamide hardly finds its way through the narrow channels. Therefore, structural properties of polymer molecules and consequently rheological properties of the solution may significantly influence flow distribution in porous media. Furthermore, expansion and contraction of streamlines are obvious in case of polyacrylamide, while, streamlines of xanthan gum and especially Newtonian fluid tend to be more uniformly distributed. Flow distribution and stream line deformation (i.e., expansion and contraction) may strongly influence overall pressure drop of viscoelastic flow through complex geometries.

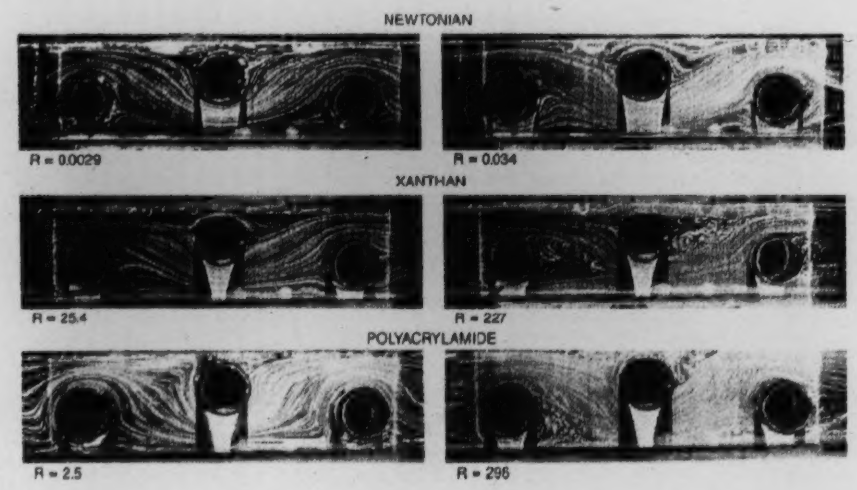

Fig. 2-9 Flow visualization for a Newtonian liquid, 1250 ppm aqueous solution of xanthan gum and a 250 ppm aqueous solution of polyacrylamide, 20°C. R is a Reynolds number (Jones et al. 1989)

Frequent expansion and contraction of flow streamlines is more obvious in flow geometries composed of circular obstacles that are show in Fig. 2-9. It is clearly observed in both geometries that converging into narrow channels results in complex deformation of fluid. In other words, a fluid element is not only sheared but also stretched in the direction of flow. Therefore, total deformation is the combination of both shear and extension experienced by fluid during flow in porous media. According to pictures shown in Fig. 2-9, flexible Polyacrylamide molecules easily deform in tortuous channels. Significant expansion and contraction of Polyacrylamide streamlines are also observed in Fig. 2-9. Therefore, polyacrylamide with highly flexible large molecules is expected to have high elongational deformation during flow in porous media. Dauben et al. (1966) suggested that frequent expansion and contraction of fluid could contribute to significant pressure drop during viscoelastic flow in porous media.

It is also observed that Polyacrylamide solution shows dramatic resistance to pass through narrow channels. While some part of xanthan solution with insignificant elastic properties passes through narrow channels even at high Reynolds numbers. Jones et al. (1989) estimated the percentage of fluid passing through narrow channels using the photographs taken during the flow. The results are shown in Fig. 2-10.

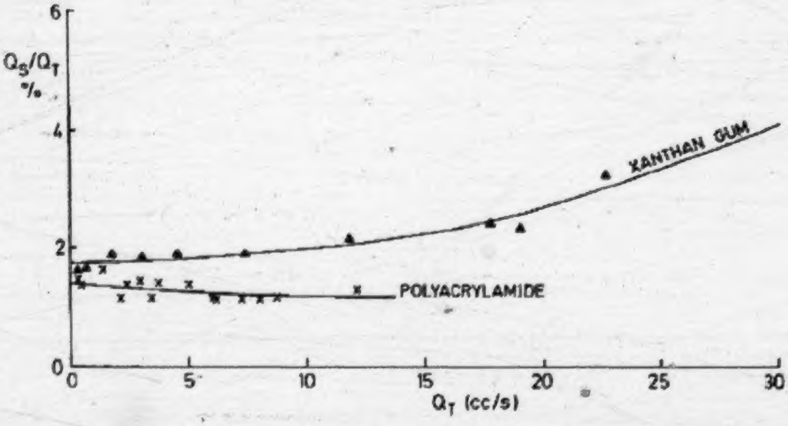

Fig. 2-10 The percentage of fluid passing through narrow channels against total flow rate for a 1500 ppm aqueous solution of xanthan gum and a 250 ppm aqueous solution of polyacrylamide, (related to flow visualization shown in Fig. 2-9) 20°C (Jones et al. 1989)

Fig. 2-10 highlights that the percentage of xanthan gum solution passing through narrow channels increases with velocity. This may be explained by shear thinning behavior of XG solution and its insignificant elastic properties. On the other hand, the percentage of polyacrylamide solution streamlines passing through narrow channels tends to remain constant. This could be explained by its highly elastic molecules that require large deformation to pass through narrow channels.

2.4.3 Deformation of viscoelastic fluids in porous media

Complexity of porous medium geometry containing tortuous channels with variable cross sectional area, results in complicated deformation of fluid. A viscoelastic fluid flowing through a packed bed experiences both extensional and shear deformation. As a result, normal and shear stresses simultaneously influence the flow behavior. During flow in porous media on each contraction and expansion, the fluid would be sheared near the wall and extended along the flow axis.

Due to tortuous flow pass in porous media, a fluid element frequently experiences convergence and divergence at the entrance and exit of narrow channels respectively.

Fluid elements accelerate during converging into pore throats while they decelerate in the second half of flow through pore throat (Khan et al. 2004). Because of extensional deformation of fluid while converging into narrow channels extensional viscosity plays a great role in resultant pressure drop. Underestimation of pressure drop by considering pure shear deformation in porous media, confirms that extensional viscosity may be a significant component of apparent viscoosity. Generally polymer solutions present shear thinning behavior. Extensional viscosity also decreases with increasing strain rate. However, Trouton value representing the ratio between extensional viscosity and shear viscosity increases with deformation rate for most of polymers. Therefore, dramatic increase of pressure drop in porous media with increasing flow rate may be an indication of the elastic effects on pressure drop.

2.4.4 Transient nature of viscoelasic flow in porous media

The size and length of polymer molecules are relatively large and are comparable to the size of pore throat and pore body. When such large molecules hit the wall in porous media they compress and deform. In order to continue to flow under the flow potential effect, polymer molecules should be relaxed and stretched (Garrocuh et al. 2006). The time required for such macromolecules to exit a pore throat or pore body is comparable to their characteristic relaxation time. It has been shown in literature (Gupta et al. 1985) that transit time for fluid passing through a pore space strongly influences flow resistance in porous media. Furthermore, variation of flow cross-section area due to tortuous nature of porous media, results in frequent contraction and expansion and consequently accelerating and decelerating of fluid elements during flow through porous media. Therefore, the following time characteristics strongly influence viscoelastic flow in porous media.

- Fluid relaxation time
- The time required for fluid to go through a contraction or expansion

Depending on the relative values of these two time variables, Sadowski et al. (1965) considered two possible situations in viscoelastic flow through porous media:

1) If the relaxation time of fluid is relatively lower than the required time to pass through contraction or expansion, no elastic effects would be observed, because fluid instantly responds to induced deformations.

2) If the fluid relaxation time compared to required time to go through contraction and expansion, is large enough then elastic effects are likely to be important.

"Ellis number" defined by Eq. 2-19 presents a criteria for the importance of elastic effects.

$$El = \frac{\mu_0/\tau_{1/2}}{D_P/V}$$

2-19

This dimensionless number has also been referred in literature as Deborah number. $\mu_0/\tau_{1/2}$ presents an estimation of required time to pass through a contraction or expansion. D_P/V gives a measure of relaxation time of fluid. Experiments conducted by Sadowski et al. (1965) showed that elastic effects are likely to be important at about El=0.1.

Since it takes longer time for each molecule to relax and restart flowing after each deformation in porous media, fluids with higher relaxation time may experience higher pressure drop while flowing through porous media. However, significant elastic features of fluid could be masked by very short transit time during flow through a pore. Dauben et al. (1966) suggested that if the relaxation time is long enough or fluid velocity is sufficiently high the fluid can pass through large opening before it has time to respond to induced stress change at the entrance. Therefore, a viscoelastic fluid tends to present viscous behavior under such conditions. They argued that fluids with longer relaxation time are likely to present viscous behavior. This is not in agreement with the argument of Sadowski et al. (1965) about the role of relaxation time on elastic effect during flow in porous media.

Gupta et al. (1985) theoretically showed that increasing Deborah number results in a maximum value of resistive forces and after a critical value of Deborah number flow resistance will start decreasing. They explained this behavior by unsteady nature of flow through porous media. In other words, increasing Deborah number initially results in higher pressure drop due to enhancing elastic effects of flow, but at sufficiently high flow rates, little time is given to stresses to build up. Therefore, fluid passes through pore body faster and consequently results in reduction of resistive forces. Although fluids with longer relaxation time may pass very fast through tortuous channels without additional deformation, it could take longer time for them to relax from a specific deformation. Therefore a detailed investigation related to role of relaxation time in viscoelastic effects is needed.

Experimental investigations have relatively confirmed the correlation between Deborah number and viscoelastic pressure drop in porous media. However, Gupta et al. (1985) suggested that Deborah number is not the only dimensionless number controlling the extra pressure loss of viscoelastic fluids in porous media. It has also been shown in literature (Kemblowski et al. 1978) that the correlation between Deborah number and product of Reynolds number with friction factor depends on the geometry of porous media. Deiber et al. (1981) conducted some flow tests through a tube with sinusoidal variable diameter and recognized the dependency of the product of Reynolds number with friction factor on the diameter change of such geometry. Gupta et al. (1985) suggested that the effect of dimensionless parameters other than Deborah number on pressure drop is also related to the transient nature of flow in porous media. They considered the case of flow through a tube with axial variation in diameter. They illustrated that due to the transient nature of viscoelastic flow in a complex geometry, dimensionless groups other than Deborah number (e.g., amplitude of diameter variations) are also important. They also showed that regardless of the value of Deborah number, under a certain values of diameter amplitude, shear thickening behavior may not be exhibited by a fluid undergoing extensional deformation.

Considering Deborah number as a criterion for importance of viscoelastic effects, the following conclusions were are made (Marshal et al. 1966):

- At velocity fields corresponding to very low values of Deborah number viscoelastic effects are negligible. It means that induced deformation rate is so low that fluid elements instantly respond to their local state of deformation. In other words, fluid elements do not remember their earlier deformation rates because they instantly deform according to the imposed velocity field. Therefore, at low shear rates, expressions related to purely viscous fluids could be used to predict pressure drop resulting from flow through porous media.

- As Deborah number increases the solid-like characteristics of polymer molecules becomes important.
- Further increase of Deborah number between 0.1 and 1 results in additional pressure drop.
- However, both the magnitude of pressure drop and the critical value of Deborah number depend on pore size distribution and uniformity of porous media.

2.4.5 Critical flow rate

Jones et al. (1989) suggested the behavior described in Fig. 2-11 for viscoelastic flow through a tortuous geometry.

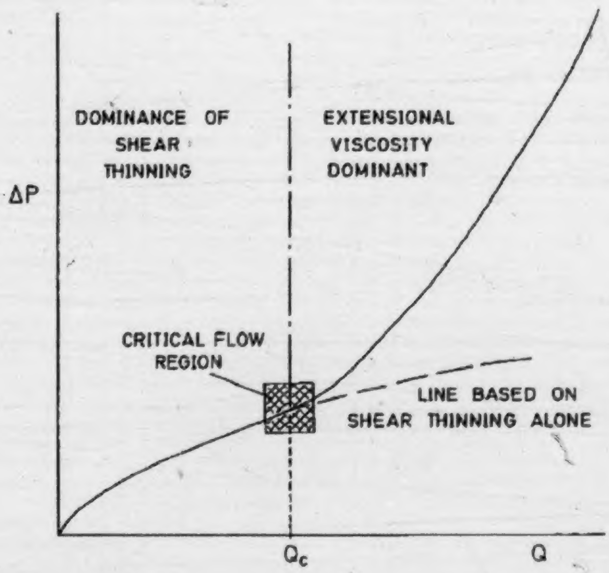

Fig. 2-11 Schematic representation of $(\Delta P, Q)$ behavior in the case of elastic liquids (Jones et al. 1989)

Fig. 2-11 highlights that at low shear rates (before reaching critical flow rate condition) pressure drop is mainly influenced by viscous forces. Shear thinning behavior is also obvious before reaching the critical flow rate. If the elastic properties of a polymer solution are negligible (e.g., xanthan gum solution) the pressure drop-flow rate profile would continue following shear thinning curve. In case of a polymer solution with significant elastic characteristics (e.g., polyacrylamide) after a certain flow rate, expansion and contraction of fluid during flow in tortuous channels, results in extra pressure drop. This behavior is known as tension thickening in literature. Therefore, in any experiment or field application this critical flow rate should be identified correctly to decide whether elastic effects are likely to be important.

According to Marshal et al. (1966), at low flow rates corresponding to very low values of Deborah number (i.e., < 0.05), viscoelastic effects are negligible. It means that induced deformation rate is so low that fluid elements instantly respond to their local state of deformation. In other words, fluid elements do not remember their earlier deformation rates. Therefore, at low shear rates, expressions related to purely viscous fluids may predict pressure drop of viscoelastic fluids in porous media. This is in agreement with the behavior presented in Fig. 2-11. As Deborah number increases the solid-like characteristic of polymer molecules becomes important and elastic effects of polymer solution (i.e., normal forces and extensional viscosity) strongly influence flow performance in porous media. Viscoelastic pressure drop in porous media dramatically increases when Deborah number exceeds the values between 0.1 and 1 (Marshal et al. 1966).

Jones et al. (1989) injected two different polymer solutions into an asymmetric geometry containing circular obstacles and obtained the following pressure drop-flow rate profiles.

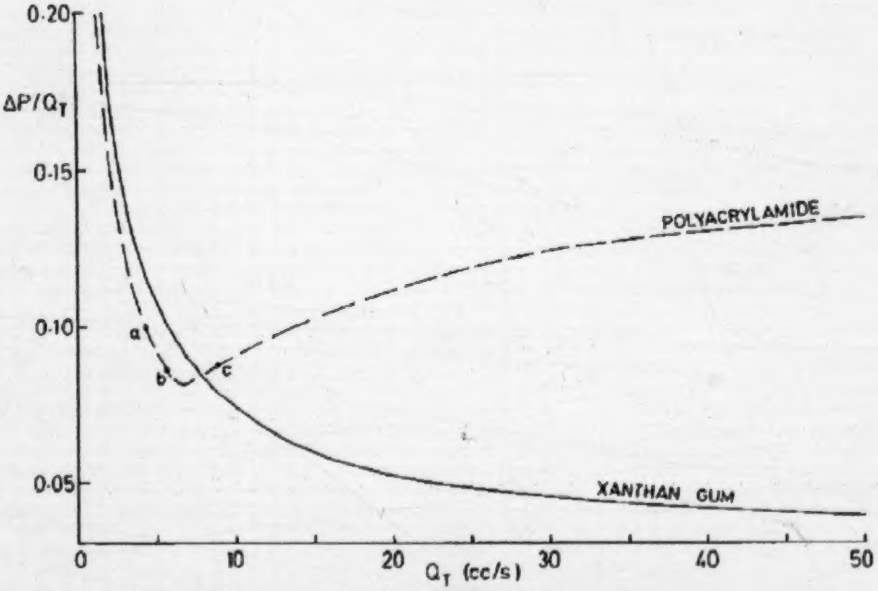

Fig. 2-12 The ratio of pressure drop to flow rate against flow rate for a 1500 ppm aqueous solution of xanthan gum and a 250 ppm aqueous solution of polyacrylamide (related to geometry shown in Fig. 2-9), 20° C (Jones et al. 1989)

Pressure drop-flow rate relationship of the two solutions is relatively similar at flow rates lower than a critical value. But after reaching that critical flow rate, the resistance forces against flow of polyacrylamide solution in tortuous channels dramatically increases. Due to shear thinning behavior of xanthan gum solution, shear viscosity controlling its flow performance considerably decreases at higher flow rates. Although Polyacrylamide presents shear thinning behavior, its pressure drop–flow rate relationship shows thickening behavior after a certain flow rate. It means that its flow behavior is not only controlled by shear stress but also Elastic forces related to its large molecules.

However, both the magnitude of pressure drop and the critical value of Deborah number depend on pore size distribution and uniformity of porous media. Due to extra pressure drop after the critical Deborah number, porous media might partially be blocked that considerably influence the uniformity of porous media.

2.4.6 Polymer wall interaction

In order to investigate retention/adsorption of polymer molecules in porous media, Sadowski (1965) compared the mechanism of gel formation in porous media during constant flow rate and constant pressure drop experiments. In constant flow rate experiments, it was observed that there is a constant tendency for removing polymer molecules from particles surfaces. According to Sadowski (1965) development of gel will not occur due to the constant disruption of any potential network structure by the bulk motion of fluid. However, at constant pressure experiment adsorption/retention of big polymer molecules will occur at reasonable flow rates. Sadowski (1965) concluded that in constant pressure drop experiment, bed permeability decreases with time because of the following reasons:

- Permeability reduction, due to any tendency toward gel formation, combined with constant pressure drop along the flow system results in continuous reduction of flow rate.
- The lower rate due to reduction of permeability, lowers the tendency to remove the polymer molecules from the particle surface.

Interaction between polymer molecules and pore space wall results in kinetic energy reduction of flow. Dauben et al. (1966) investigated this phenomenon by measuring apparent viscosity of different sample solutions with different molecular weights during flow through packed beds with different glass bead sizes. Fig. 2-13 demonstrates different profiles obtained from conducted core flow experiments.

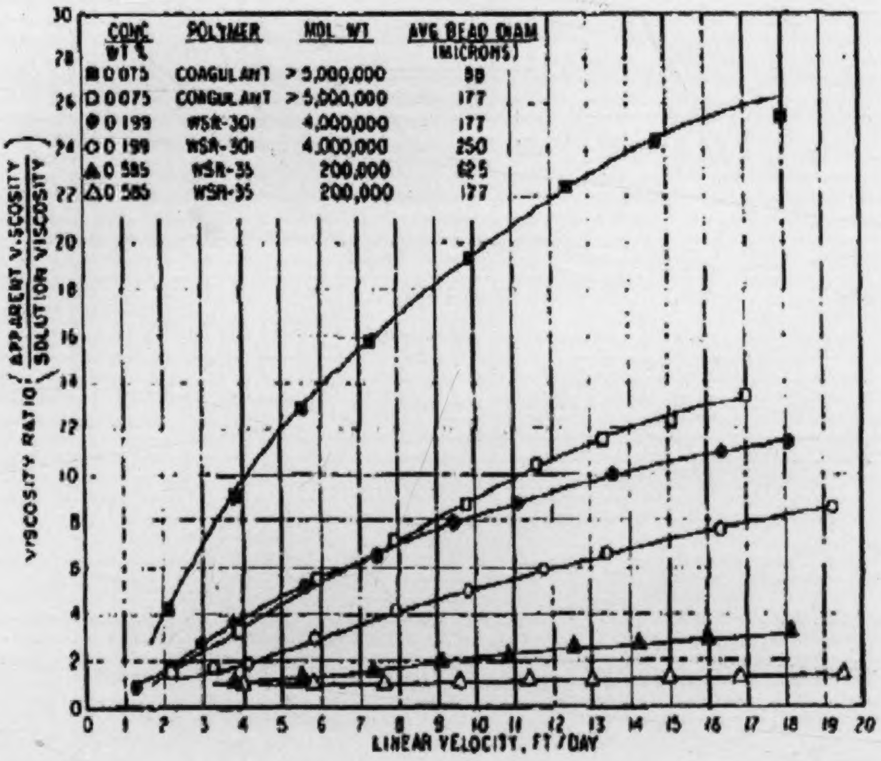

Fig. 2-13 Flow performance curves illustrating effect of bead size on viscosity ratio (Dauben et al. 1966)

It is observed that apparent viscosity is considerably higher in case of smaller pore size and higher molecular weights. Increasing interaction between large polymer molecules and pore body results in extra pressure loss. However, molecular weight also influences the relaxation time of fluid that could consequently affect the apparent viscosity of fluid in porous media. Smaller bead size which implies low permeability also increases the polymer-wall interaction. Deborah number is higher in case of smaller bead size that may result in dominance of elastic resistive forces.

Fig. 2-14 shows that increasing polymer molecular weight significantly increases the pressure drop. Dauben et al. (1966) explained that extra pressure drop in their experiments is mainly due to combined effects of polymer wall interactions as well as viscoelastic effects. Polymer molecular weight influences rheological properties of polymer solution (e.g., shear and extensional viscosity and relaxation time).

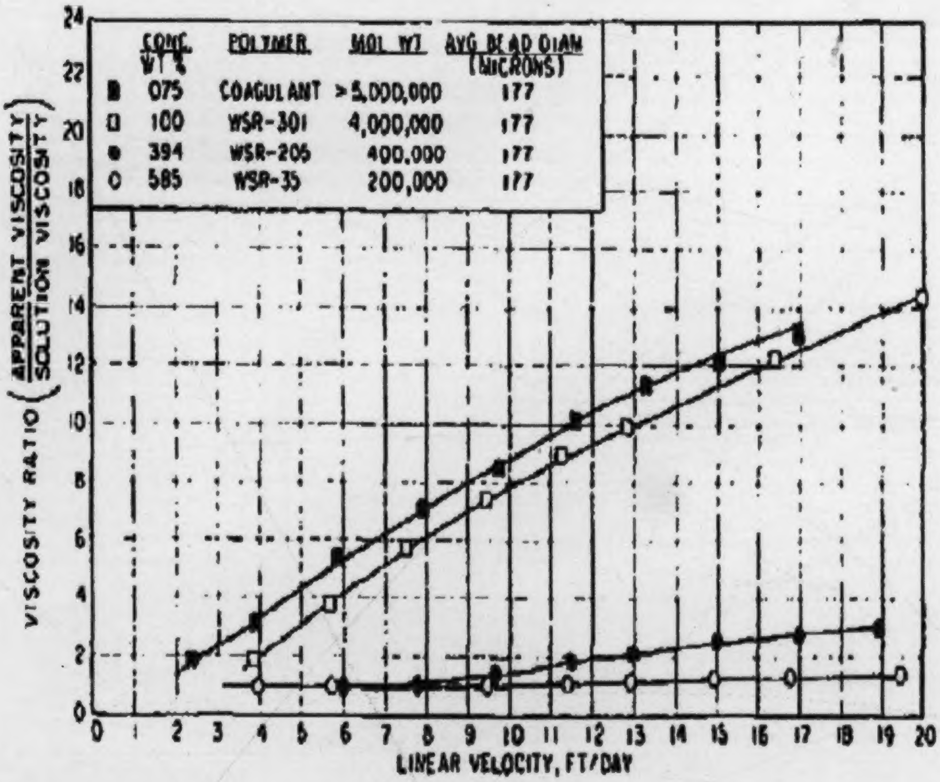

Fig. 2-14 Flow performance curves illustrating effect of molecular weight on viscosity ratio (Solution Viscosities, 4 to 5 cp) (Dauben et al. 1966)

Merrill (1963) suggested that polymer wall interaction becomes important when channel diameter is less than 20 times of the particle diameter. Effective diameter of entangled group of coils formed by polymer macromolecules could be many times larger than calculated single coil size. Therefore, flow of such large particles through porous media with pore openings around 5 to 10 microns may be accompanied by kinetic energy reduction due to polymer molecule wall interaction (Dauben et al. 1966). According to Chiappa et al. (1999) during polymer flow in porous media some polymeric materials adsorb in porous media resulting in permeability reduction. Martins et al. (2005) experimentally investigated this phenomenon. They measured the core permeability by a

Newtonian fluid before and after injection of polymer solution. Reduction of permeability after the test indicated that some portion of injected polymer remains in pore space because of adsorption of polymer molecules in porous media. However, Dauben et al. (1966) showed that pressure drop remains constant at fixed shear rate and concluded that even if plugging happens during the core flow test it does not continuously reduce the permeability.

Khan et al. (2004) measured the permeability of the core samples after injection of Polymer solutions and quantified the resulting formation damage (Table 2-1).

Table 2-1 Formation damage measured after the flow of polymer solutions (Khan et al. 2004).

	PHPA	**Xanthan Gum**
Fluid Concentration lb/bbl	**Formation Damage %**	**Formation Damage %**
0.50	2.50	21.19
1.50	3.79	25.41
3.00	5.33	28.39

It is clear from their results that the formation damage created by XG is significantly higher than the percentage of permeability reduction in case of PHPA. However, it is interesting that damaging characteristics of XG with insignificant elastic properties is considerably more than PHPA solution that is a highly elastic fluid. If flow rate is low enough highly flexible PHPA molecules can easily deform during flow through tortuous channels of porous media. This may be an explanation for lower formation damage in case of PHPA. In order to flow through tight and tortuous flow channels of porous media, polymer molecules must have the ability to deform sufficiently (Dauben et al. 1966). Therefore, polymer solution must have enough viscoelastic characteristics to be suitable for propagation through porous media. This is in good agreement with the experimental data presented in Table 2-1 demonstrating a significant formation damage resulting from flow of XG solution with little or no elastic effects.

The following reasons could be suggested for higher formation damage in case of XG solution compared to PHPA solution.

1) PHPA molecules are flexible and easily deform during flow in complex geometries while rigid rod-like XG molecules hardly deform tortuous geometries and are more likely to trap the narrow channels of flow geometry.
2) PHPA solution tends to bypass narrow channels of porous media while according to Fig. 2-8 and Fig. 2-9, XG solution shows a considerable tendency to pass through narrow channels that consequently increases the chance of XG molecules to plug some part of tortuous flow geometry (e.g., porous media).

2.4.7 Pressure due to flow of viscoelastic fluids through complex geometries

Basically, the pressure loss resulting from the flow of viscoelastic fluids in porous media is a function of physical properties of porous media and material functions of fluid. A detailed investigation is needed about the role of fluid viscoelastic properties on additional pressure loss in porous media that can be treated as an internal filter cake building. Dauben et al. (1966) observed unexpectedly high flow resistance under certain conditions in some core flow experiments. It was also observed in their experiments that flow rate, pore size, polymer molecular weight and concentration considerably influence such behavior of viscoelastic flow in porous media.

Various experimental investigations presented in the literature (e.g., Khan et al. 2004; Martins et al. 2005) shows that the pressure drop due to flow of a viscoelastic fluid through porous media is higher than the values predicted by Darcy equation. Jones et al. (1989) conducted some flow tests to observe the real profile of pressure drop-flow rate relationship due to the flow of viscous and viscoelastic polymer solution through complex geometries. Profiles resulting from fluid flow through two different geometries described in Fig. Fig. 2-15 are presented in Fig. 2-16 and Fig. 2-17.

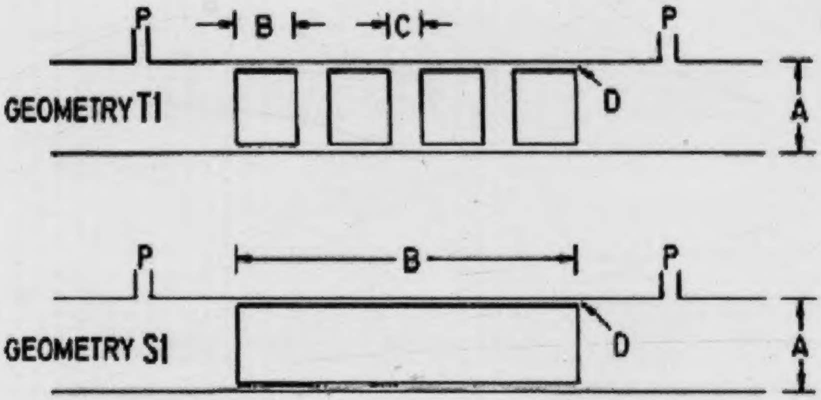
P
B
C
P
GEOMETRY T1
D
A
P
B
P
GEOMETRY S1
D
A

Fig. 2-15 Schematic diagram of the model geometries (Jones et al. 1989)

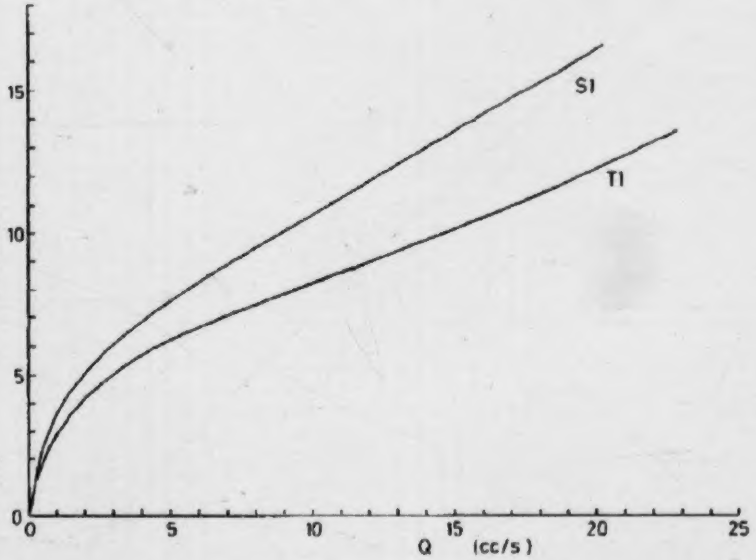

Fig. 2-16 Experimental data for a 1600 ppm aqueous solution of xanthan gum, 20°C (Jones et al. 1989)

Fig. 2-16 highlights that XG that is a viscous polymer solution with negligible elastic properties presents shear thinning behavior in both geometries. However, there is some indication of upturn in the curves at the higher flow rates.

Considering the geometries used in this experiment, the extent of narrow channels between the block(s) and the wall in S1 is relatively longer than T1 case. Therefore, based on conventional fluid mechanics higher pressure loss is expected in case of S1 that is in good agreement with observed profiles in case of XG solution. Therefore, pressure drop of XG in complex geometries such as porous media may be mainly due to viscous effects. It means that expansion and contraction of fluid streamline may not have significant influence on its flow in porous media.

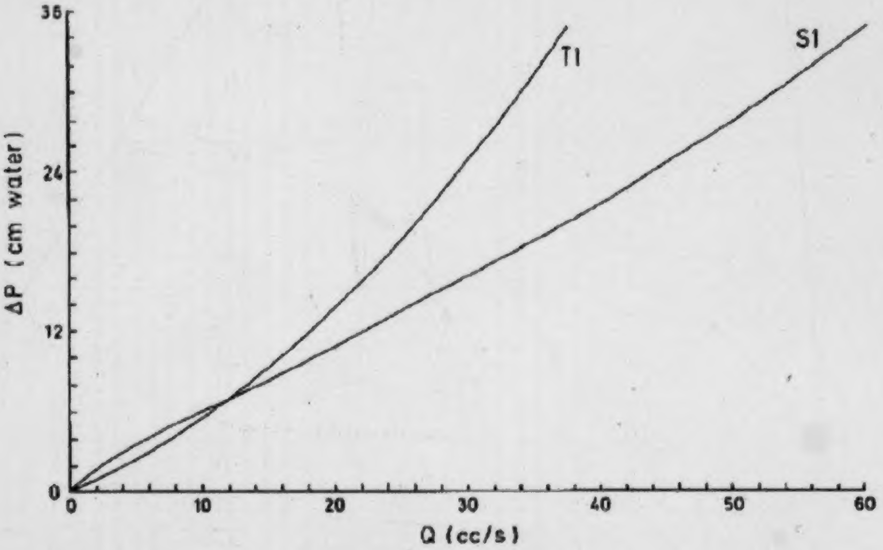

Fig. 2-17 Experimental data for a 50 ppm aqueous solution of polyacrylamide, 20° C (Jones et al. 1989)

Fig. 2-17 shows that in case of polyacrylamide tension thickening behavior is obvious in both curves especially at higher rates. However, there is a slight indication of shear thinning behavior in case of S1 geometry at low shear rates. Even at low shear rates, Polyacrylamide does not present shear thinning behavior during flow in T1 geometry. Therefore, depending on special features of flow geometry pseudo plastic behavior of polymer solutions may be masked by strong viscoelastic effects. Although, the percentage of narrow flow passes in T1 geometry is relatively lower that S1 geometry, it is observed that measured pressure drop in T1 is considerably higher than recorded pressure loss in S1 geometry. Jones et al. (1989) explained that elongational flow induced by porous nature of T1 geometry results in higher pressure loss due to extensional viscosity effect. However, at low shear rates pressure drop of S1 geometry is higher than T1 geometry. It means that elastic effects do not have significant influence on flow behavior of polyacrylamide solution at low shear rates.

Khan et al. (2004) measured the pressure drop resulting from flow of PHPA and XG solutions in a simulated porous media. The characteristic deformation rate related to medium properties, density and flow rate of fluid was approximately 105 sec^{-1}. They measured the fluid viscosity at this shear rate and finally the theoretical value of pressure loss was calculated using Darcy equation. Table 2-2 presents a comparison between the measured pressure data and corresponding calculated values.

Table 2-2 Measured and calculated pressure loss values (Khan et al. 2004)

	PHPA			**Xanthan Gum**		
Fluid	**Meas.**	**Calc.**		**Meas.**	**Calc.**	
Conc.	**Press. Loss**	**Pres. Loss**	**% Diff.**	**Pres. Loss**	**Pres. Loss**	**% Diff.**
lb/bbl	**Psi**	**Psi**		**Psi**	**Psi**	
0.50	3.29	3.01	9.3	7.09	6.77	4.72
1.50	13.69	9.35	46.4	17.24	15.39	11.6
3.00	32.72	24.9	31.4	37.33	29.26	27.3

The measured pressure loss is higher than predicted values using Darcy equation. Although, the pressure loss is lower in case of PHPA because of its lower viscosity, the percentage of difference is relatively higher in case of PHPA. The degree of formation damage induced by PHPA solution is relatively lower compared to XG solution, while, deviation from Darcy equation is more dominant in case of PHPA solution compared to XG solution. It is in good agreement with previous discussions related to contribution of viscoelastic effects on additional pressure drop.

Different scenarios have been presented in literature to explain such extra pressure loss of viscoelastic flow through porous media. Extensional viscosity may be the main reason of extra pressure loss in such flow configurations (Naverrete et al. 2000). Experimental investigations show that a great proportion of pressure loss of viscoelastic flow in porous media is related to elastic forces and elongational viscosity. Marshal et al. (1966) suggested that additional pressure drop of viscoelastic flow in porous media is mainly due to viscoelastic effects. Svendsen et al. (1998) showed the establishment of internal filter cake by coil tubing drilling fluid with high extensional viscosity. Durst et al. (1987) suggested that about 75% of pressure loss of drilling fluid flow in porous media could be related to extensional resistive forces. However, it should be noted that both extensional viscosity and normal stress are likely to be important when flow rate exceeds a critical value. Naverete et al. (2000) suggested that the flow of XG solution is mostly influenced by shear viscosity while flow of PHPA solution through porous media is dominated by extensional viscosity especially at high enough shear rates. Their result is relatively in good agreement with what Khan et al. (2004) concluded from their experiments. Therefore, it could be concluded that viscoelastic effects such as extensional viscosity and normal forces play an important role in extra pressure drop resulting from flow of PHPA solution in porous media.

Measured value of pressure gradient along the porous media at a certain flow rate could be used to estimate apparent viscosity by Darcy equation. Fig. 2-18 demonstrates the behavior of various polyox solutions in porous media. At low shear rates, viscosity ratio of all solutions are relatively the same (around 1). This means that the factors responsible for extra pressure drop do not play a significant role at low shear rates. The viscoelastic effects that may be responsible for higher pressure drop are more pronounced at higher flow rates. Permeability impairment could be important even at low shear rates, while according to Fig. 2-18 the deviation from Darcy law is insignificant at low shear rates. Therefore, permeability impairment is not likely to be important in these experiments. Dauben et al (1966) observed significant reduction of mobility of polyethylene oxide solutions in porous media under certain conditions. They argued that anomalous viscosity effect is the main reason for such behavior because polyethylene solutions appeared not to plug the matrix.

Furthermore, the deviation between different curves representing specific experimental conditions is more pronounced at higher shear rates. It means that the fluid properties as well as flow geometry strongly influence pressure drop especially at higher shear rates.

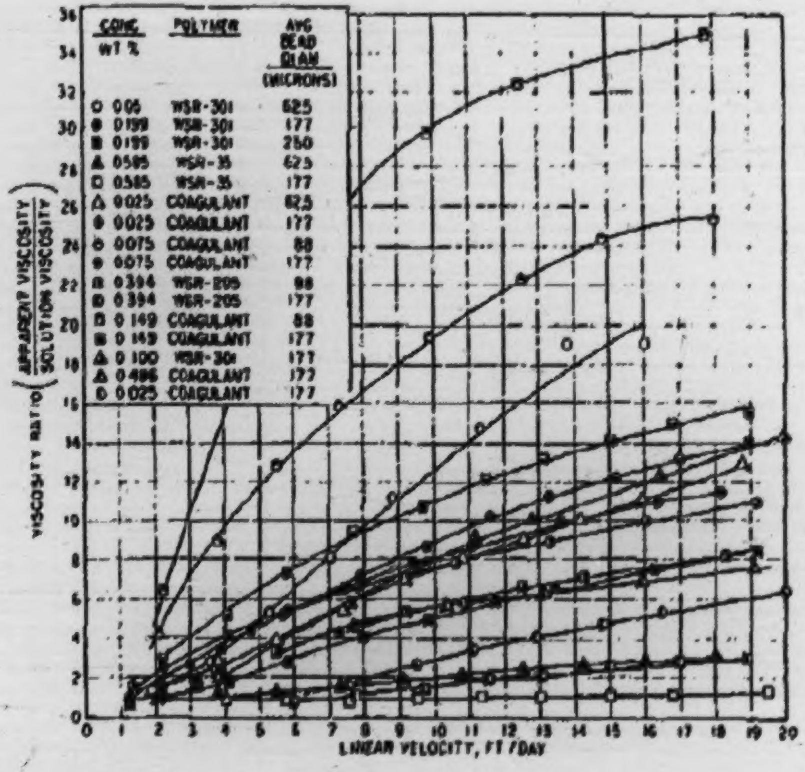

Fig. 2-18 Flow performance of various polymer solutions in porous media (Dauben et al. 1966)

2.5 Quantitative analysis of viscoelastic flow through porous media

In order to model polymer solutions flow into the reservoir rock, viscoelastic characteristics of such fluids as well as porous media properties should be correctly taken into consideration. The following factors should be considered in modeling viscoelastic flow through porous media:

- Shear viscosity of non-Newtonian fluids strongly depended on shear rate.

- Equivalent deformation rate in porous media is a function of flow rate and porous media properties.
- Viscoelastic parameters such as relaxation time, Deborah number, normal stress differences and Trouton ratio strongly influence flow performance of polymer solutions in porous media.
- Extensional viscosity of polymer solutions could contribute to extra pressure loss during flow through porous media.
- Adsorption/retention of polymer molecules in porous media may result in permeability impairment.

2.5.1 Deborah number

The relation between relaxation time of each material and characteristic time of experiment is expressed by dimensionless Deborah number (De). This number is a measure of viscoelasticity of a flow system. A viscoelastic material in an experiment with a very high Deborah number behaves like an elastic solid while it will present purely viscous behavior in very low Deborah number.

Savins (1969) showed that in order to consider the elastic effects, the value of pressure drop calculated in the absence of elastic effects should be multiplied by a factor of$[1 + \beta De^2]$. Where, β is a constant parameter. The following factors influence the value of Deborah number related to a specific core flow experiment (Garrouch et al. 2006):

- Polymer concentration
- Molecular weight of polymer
- Viscosity at zero shear rate
- Fluid superficial velocity
- Characteristic grain size diameter of the rock

Bird et al. 1987 defined Deborah number, De, by:

$$De = \frac{\mu_0/\tau_{1/2}}{D_p/u_0}$$

2-20

Where, μ_0, $\tau_{1/2}$, D_p , and u_0 are the zero shear rate viscosity, the value of the shear stress at which the viscosity is half of μ_0 , the particle diameter and the superficial velocity, respectively. D_p/u_0 presents an estimation of required time to pass through a contraction or expansion. $\mu_0/\tau_{1/2}$ Gives a measure of relaxation time of fluid. Sadowski et al. (1965) experimentally showed that elastic effects are likely to be important at Deborah number of about 0.1. Garrouch et al. (2006) and Marshal et al. (1966) used estimated longest relaxation time of polymer solution to calculate the Deborah number defined by:

$$De = \frac{\theta_0 u_0}{D_p \varphi}$$

2-21

$$D_p = \sqrt{\frac{150\,(1-\varphi)^2 k}{\varphi^3}}$$

2-22

2.5.2 Pressure drop-flow rate relationship

Flow of polymeric solutions has a great significance in some applications such as water flooding for secondary oil recovery and filtration of polymeric drilling fluids into porous media. Therefore, knowing the exact relationship between flow rate and pressure drop for the flow of viscoelastic fluids in porous media is very important.

2.5.2.1 Equivalent deformation rate in porous media

Rheological parameters of non-Newtonian fluids (e.g., extensional and shear viscosity) are a function of equivalent deformation rate. Many correlations have been presented in literature to predict the equivalent shear rate in porous media as a function of flow rate and rock physical properties. Since the shear rate in each pore-throat is strongly related to the pore-throat diameter, in order to define a characteristic deformation rate through a porous media, the pore size distribution of rock should be considered. . In other words shear rate distribution in porous media is strongly related to pore size distribution. McKelvey et al. (1962) gave the following expression for wall shear rate of a simple power law flow in a pipe:

$$\dot{\gamma} = \frac{3n+1}{4n}\frac{8V}{D}$$

2-23

By replacing the velocity of fluid, V, with $G/_{\rho\varphi}$ and D by four times of the hydraulic diameter, Christopher et al. (1965) modified this equation to estimate the equivalent shear rate in the packed bed:

$$\dot{\gamma} = \frac{3n+1}{4n}\frac{12\,G}{\rho(150\,k\,\varphi)^{1/2}}$$

2-24

In this equation G is the fluid flux in gram.cm-2.sec-1, and k is permeability in m2, n is the flow behavior index, φ is the void fraction (i.e., porosity), $\dot{\gamma}$ is the wall shear rate in sec-1 and ρ is the fluid density in gr/cc. Dauben et al. (1966) suggested the following equation to estimate the equivalent shear rate in porous media:

$$\dot{\gamma} = \frac{12\sqrt{2}V(1-\varphi)}{D_p\varphi}$$

2-25

Eq. 2-26 presents another expression for equivalent deformation rate that has been derived using Blacke-Kozeny model (Jones et al. 1981; Yuan et al. 1981).

$$\dot{\gamma} = \left[\frac{3n+1}{4n}\right]^{\frac{n}{n-1}}\frac{4V}{\sqrt{8k_f\varphi}}$$

2-26

This expression also shows that equivalent shear rate is a function of both fluid and medium properties. n is the power-law exponent that could be obtained by calculating the slope of log-log plot of measured shear stress versus shear rate. In order to consider the effect of permeability impairment on overall pressure drop, the flushed permeability (k_f) has been used in this equation.

Chauveteau (1982) gave the following equation for average shear rate in porous media.

$$\dot{\gamma} = \frac{4\,\alpha\,q}{A\,(8k\varphi)^{0.5}}$$

2-27

Where, A and q are cross sectional area and flow rate respectively. α is the material constant that is 1.7 for glass beads.

All of these equations highlight that the shear rate depends on rheological properties of fluid (i.e., power law exponent "n") as well as flow geometry.

2.5.2.2 Newtonian flow through porous media

Flow of Newtonian fluids through porous media is simply modeled by Darcy equation.

$$\frac{Q}{A} = \frac{k}{\mu} \cdot \frac{\Delta P}{L}$$

2-28

According to Darcy equation the pressure loss for a specific flow system is linearly proportional to flow rate. Laminar flow of a Newtonian fluid in porous media has also been described by the following semi-empirical expression known as Blake-Kozeny equation (Bird 1960).

$$V = \frac{\Delta P\, {D_p}^2 \varphi^3}{150 L\mu (1-\varphi)^2}$$

2-29

This equation has been derived using "capillary model". Therefore, the effect of expansion and contraction of fluid during flow through tortuous channels of porous media has been disregarded in its derivation. However, this expression may be applicable to predict the behavior of viscoelastic flow in highly permeable and porous media where frequent expansion and contraction of fluid streamline is negligible. Christopher et al.

1965 suggested the following expression for the permeability of a packing with thwe porosity of.

$$k = \frac{{D_p}^2 \varphi^3}{150(1-\varphi)^2}$$

2-30

2.5.2.3 Non-Newtonian viscous flow in porous media

It has been observed experimentally that there is a non-linear relationship between pressure drop and flow rate of a non-Newtonian fluid in porous media. This non-linearity is mainly due to dependency of shear viscosity on flow rate. Robert et al. (1965) used power law model to modify Blake-Kozeny equation for flow of a non-Newtonian fluid through a porous media composed of uniform spherical particles.

Sadowski et al. (1965) proposed an approximate way to characterize flow performance of non-Newtonian fluids in complicated flow geometries. In this method they considered the following parameters:

1. Zero-shear limiting viscosity (μ_0): experimental data show that viscosity of non-Newtonian fluids tends to a limiting value as shear rate goes to zero.
2. Characteristic time (t_c): some of viscoelastic effects like recoil and relaxation phenomena have to be characterized by one or more relaxation time that could be used to designate the flow region where elastic effects are likely to be important.
3. Slope of a log-log plot of viscosity versus shear rate in the power law region (α).

These parameters were used to correlate experimental data of pressure drop through packed beds at constant flow rate.

Van Poolen et al. (1969) and Willhite et al. (1986) presented the following expression as a non-linear relationship between pressure loss and flow rate of a non-Newtonian fluid in porous media:

$$\Delta P = F \frac{Q^{m+1}}{A^{m+1}} L$$

2-31

In this expression m is a power law constant that accounts for fluid non-Newtonian properties. F is an empirical constant related to medium properties (i.e., porosity, permeability and tortuosity).

Considering the non-linear relation between pressure gradient and fluid superficial velocity, a general form for non-Newtonian flow through porous media is given by:

$$v^n = (\frac{k}{H})\frac{\Delta P}{L} \tag{2-32}$$

The parameter H accounts for non-Newtonian viscous behavior of fluid as well as flow geometry. Different expressions have been presented for H in literature as follows:

Bird et al. (1960):

$$H = m\left[2\left(\frac{25}{12}\right)^n\left(\frac{3n+1}{n}\right)^n(3)^{n+1}/150\right]\left(D_p\right)^{1-n}(\varphi)^{2(n-1)} \tag{2-33}$$

Christopher et al. (1965):

$$H = \frac{m}{12}\left(\frac{9n+3}{n}\right)^n(150k\varphi)^{(1-n)/2} \tag{2-34}$$

Sadowski et al. (1965):

$$\frac{1}{H} = \frac{1}{\mu_0}\left[1 + \left(\frac{4n}{2n+1}\right)\left(\frac{{\tau_{RH}}^{(1-n)/n}}{\tau_{1/2}}\right)\right], \tau_{RH} = \left[\varphi\, D_p/6(1-\varphi)\right]\frac{\Delta P}{L} \tag{2-35}$$

Teeuw et al. (1980):

$$H = 2\, m\, k^{(1-n)/2}\left(\frac{3n+1}{\varphi n}\right)^n\left(\frac{\varphi}{8}\right)^{(n+1)/2} \tag{2-36}$$

It has been shown that elastic effects are likely to be important in viscoelastic flow through porous media. However, viscoelastic properties of fluid are not considered in these models. Therefore, deviation of predicted values of pressure drop from experimental data may be due to viscoelastic effects.

2.5.2.4 Viscoelastic flow through porous media

Extensional viscosity of Newtonian fluid is three times of its shear viscosity. Due to low values of normal force induced by Newtonian fluids, the effect of extensional viscosity on pressure drop of such pure liquids without any structure in porous media is neglected. Extensional viscosity of some viscoelastic fluids may be higher than their shear viscosity by several orders of magnitudes. Therefore, elongational deformation of such fluids in porous media may result in extremely high pressure loss that very often leads to formation of internal cake.

Sadowski et al. (1965) modified Eq. 2-35 and 2-32 to account for elastic effects and presented the following expression:

$$\left(\frac{\Delta P}{\rho v^2}\right)\left(\frac{D_p}{L}\right)\left(\frac{\varphi^3}{1-\varphi}\right)=\frac{180}{\left(\frac{D_p v\,\rho}{\mu_0}\right)\left(\frac{1}{1-\varphi}\right)\left[1+\frac{4}{\alpha+3}\left(\frac{\tau_{RH}}{\tau_{1/2}}\right)^{\alpha-1}-5\left(\frac{\mu_0 v}{D_p\tau_{1/2}}\right)\right]} \tag{2-37}$$

This expression highlights that pressure drop increases by increasing Deborah number. In other words elastic resistive forces are more pronounced at higher flow rates and fluid relaxation time.

Savins (1969) showed that purely viscous pressure drop should be multiplied by a factor of $[1+\beta(N_{DEB})^2]$ to account for elastic effects in porous media.

Massarani et al. (2001) presented a constitutive equation for the resistive force based on a general capillary model for the flows in porous media. Martins et al. (2005) used the equation given by Massarani et al. (2001) to correlate pressure drop of some polymeric solutions to first normal stress difference or Trouton ratio of the solutions:

$$\left(\frac{\Delta P}{L}\right)=\frac{Mq^n}{k^{\frac{n+1}{2}}}\left[1+C_i\frac{M_i}{M}\left(\frac{q}{\sqrt{k}}\right)^{n_i-n}\right] \tag{2-38}$$

Where, the (M_i, n_i) parameters represent (M_1, n_1) or (M_2, n_2) values depending on the adopted viscoelastic focus (N_1 or Trouton).

Garrouch et al. (2006) suggested some empirical models for viscoelastic fluid flow in porous media by using longest relaxation time, θ_0, of the polymers.

$$v = \left[\frac{\sqrt{k\varphi}}{\psi\theta_0}\right]^{\frac{1}{\bar{n}-1}} \cdot \left[\frac{\Delta P}{L}\right]^{\frac{1}{\bar{n}}}$$

2-39

Here, ψ is an empirical constant and $\bar{n}$ is an average porous medium power-law constant.

CHAPTER 3

Experimental program

Experimental program consists of: (1) Preparing aqueous solutions of different grades of polyox and its blends at different concentrations (2) Rheological characterization of polyox solutions (3) core flow experiments using radial and linear cells to investigate the influence of elastic properties of polyox solutions on pressure drop in porous media.

3.1 Materials used for the preparation of polymer-based fluids

The polymers used in this research study; were supplied at no cost by Dow Chemical Company. These polymers were different grades of Polyethylene Oxide (Polyox) that is a water-soluble resin (WSR). Five different grades of polyox in powder form were used in this study. Table 3-1 lists the approximate molecular weight of Polyox grades.

Table 3-1 Polyox grades with different molecular weights

Polyox Grade	Approximate Molecular Weight
WSR N-80	200,000
WSR-205	600,000
WSR-1105	900,000
WSR-301	4,000,000
WSR-308	8,000,000

Polyox grades are produced in the form of white to off-white, free flowing powder with a characteristic ammoniacal odor. The pH of aqueous solution of these grades at 25 deg C is between 8 to 10.

3.2 Dissolving polyox in water

The most important step in the entire dissolving operation of Polyox water-soluble resins takes place in the first few seconds-separating the individual resin particles from each other. Polyox resins are instantly wettable in water. If Polyox powder is not properly dispersed, the partially dissolved, wetted particles will agglomerate and form gels that may never dissolve.

Aqueous Polyox solutions with concentrations ranging from 1 wt% to 10 wt % were prepared by dissolving respective amount of the polymer with specific mixing ratio in required volume of de-ionized water. Hamilton-Beach overhead malt mixer was used to dissolve large Polyox molecules directly in water. Clumping up of the polymer is possible if the rate of addition is too high. Therefore, the powder was added slowly to the water. In each case the stirring was continued until the solution appeared to be homogeneous. The remaining air bubbles were removed out of solution by a vacuum pump.

To prevent shear degradation, the lowest RPM of the mixer was selected for dissolving of the polyox solutions.

3.3 Procedure for preparation polyox solutions with similar shear viscosity and different viscoelastic properties

The following procedures were followed for preparation of aqueous polyox solutions with similar shear viscosity (i.e., similar average molecular weight) and different viscoelastic properties (i.e., different molecular weight distribution).

1. Specification of the average molecular weight

Five polyox grades used in the experimental program were listed in Table 3-1. Each polyox grade has a certain average molecular weight. It was assumed that these grades have relatively narrow molecular weight distribution. The polyox grade with medium molecular weight (WSR 1105), among other grades, was considered to be the polyox blend with the narrowest molecular weight distribution. Polyox grades were available with molecular weights higher and lower than the selected grade (WSR 1105). Therefore, it was possible to prepare different blends with varying molecular weight distribution with average molecular weight equal to that of the selected grade (WSR 1105).

2. Calculation of the mass fraction components of the blend

Aqueous solutions of different polyox grades were prepared at a constant concentration (5 wt %). Shear viscosity vs. shear rate profile of these grades were determined (see Fig. 4-1). It was seen that there is a linear relationship between zero shear viscosity and average molecular weight of polyox grades (Fig. 4-5). This linear profile was used to estimate the average molecular weight of a polyox blend with known zero shear viscosity. A new equation (Eq. 4-4) for predicting average molecular weight of polymer blends was proposed. It was shown that predicted values of average molecular weight for blended polyox samples using Eq. 4-4 are in good agreement with experimental data (Fig. 4-6). Therefore, Eq. 4-4 was used to estimate the mass fraction of different components of the blend to obtain a certain value of average molecular weight.

In order to quantify the broadness of the molecular weight distribution of each blend, Eq. 4-6 was used for rough estimation of polydispersity value defined by M_w/M_n. It is expected that the higher the value of polydispersity ratio the more elastic will be the behavior of the polymer blend.

3. Specification of shear viscosity and concentration

Darcy equation in radial systems was used to specify the maximum viscosity of the polyox solutions for each core flow experiment. The pressure drop values due to the flow of water through the radial pack at different flow rates were also measured. It was assumed that pressure drop due to the flow of polyox solutions through the pack is around the measured values for water multiplied by the ratio of solution viscosity to water viscosity. Therefore, based on pressure capacity of pump and core holder, the maximum allowable viscosity for polyox solution was specified. Considering the calculated maximum shear viscosity related to each porous media, concentration of the solutions was selected (3 wt % for 8.9 Darcy pack and 1-1.5 wt% for 0.12 Darcy pack).

4. Preparation of the solution

In order to prepare aqueous solutions of blended polyox samples, required amount of each polyox grade was specified according to the concentration of the solution and mass fraction of each component of the blend (see Table 4-1Table 4-2). For example in order to prepare 3 wt % aqueous solution of sample 2, 2.25 gram WSR-N80, 4.5 gram WSR 1105 and 2.25 gram WSR 308 were dissolved in 291 cc of de-ionized water. Polyox grades were respectively added to water from high to low molecular weight. Initially respective amount of high molecular weight samples were gradually added to the mixing water. The stirring was continued until the solution appeared to be homogeneous. Finally, required amount of lower molecular weight samples were gradually added to the mixing solution. Stirring was continued at lowest RPM of the mixer to prevent shear degradation.

3.4 Rheological tests

All rheological tests were conducted by a rotational rheometer (VOR, Bohlin Instruments) with cone and plate geometry at room temperature (see Fig. 3-1). Sample fluid was placed in the 0.15 mm gap between cone and plate.

Fig. 3-1 Bohlin rheometer used for rheological characterization

To have more accurate results, excess sample was trimmed off to prevent additional inertial and viscous forces to be applied on the rotating plate (cone). Fig. 3-2 explains the correct way of sample loading.

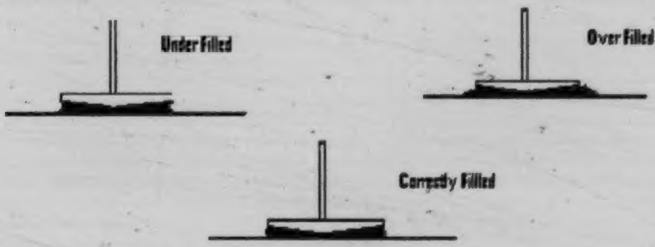

Fig. 3-2 Sample loading for Cone and plate measuring geometry

Sample solutions were characterized by four different rheological tests namely. viscometry, relaxation, oscillation and creep-recovery that are described in the following section.

3.4.1 Viscometry

In the viscometry mode of operation, shear stress as well as normal force applied on the fluid sample is measured in simple Shear flow. Shear viscosity is related to shear stress and shear rate by Eq. 2-1:

The viscosity of each sample was measured at different shear rates ranging from 0 to 1200 1/s. The shear viscosity-shear rate profile shows different parts of Newtonian (i.e., the low shear Newtonian plateau) and non-Newtonian (i.e. shear thinning) behavior (see Fig. 4-1).

If a sufficiently large strain is applied, it is possible to break the structure (i.e., the elastic part) of a viscoelastic material, resulting in purely viscous flow that is the principle of the viscometry tests. However, at low strains the elastic component strongly influences flow behavior of viscoelastic materials. Therefore, proper rheological tests including relaxation, oscillation and creep-recovery are required for characterizing viscoelastic behavior of polymeric systems.

3.4.2 Oscillation test

Basically in oscillation test a constant amplitude strain is applied on the sample at different frequencies. By measuring the stresses in each cycle both elastic and viscous modulus (G' and G") could be measured as well as the phase lag between viscous and elastic modulus(δ).

By applying a sinusoidally varying stress to a sample, a sinusoidally varying strain (and vice versa for applied strain) response will be induced. The stress applied on a Hookean solid is related to strain and modulus (G) by:

$$\tau = \gamma \times G \qquad \text{3-1}$$

For a pure solid the shear stress is proportional to strain, whereas for a pure liquid the stress is proportional to the strain rate.

In the case of a pure "Solid", since the strain is directly related to the stress, it will be at a maximum when the stress is a maximum and zero when the stress is zero. The strain response is said to be totally in phase with the applied stress (i.e., the phase angle (δ) =

0°) (see Fig. 3-4). If the material is a pure viscous "Liquid", it will be the strain rate that is exactly following the stress. It can be seen in Fig. 3-3 that the strain alternates between a positive and negative extreme accelerating and decelerating between these two values. Therefore, when the strain is at a maximum the rate of change of strain will be zero, likewise when the strain is zero, the rate of change will be a maximum. The resultant strain will therefore be totally (90°) out of phase to the applied stress (see Fig. 3-3).

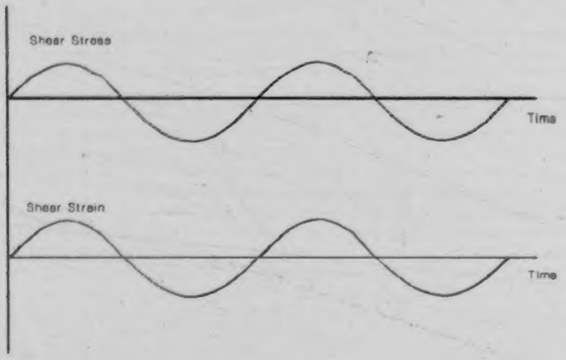

Fig. 3-3 Strain response of a solid

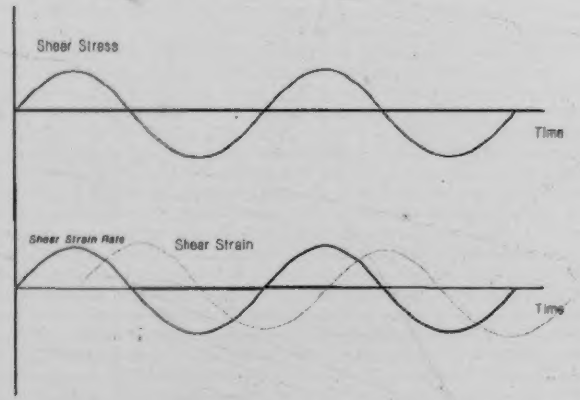

Fig. 3-4 strain response of a pure liquid

The differences of phase between the stress and strain waves in one complete cycle of the sine wave are considered as the "Phase angle" (δ). Therefore, δ is 0 and 90 degrees for pure solid and pure liquid respectively. Flow behavior of viscoelastic materials are influenced by combination of viscous and elastic effects and so the measured phase angle will be somewhere between 0° and 90°. The closer to 90°, the more fluid like the behavior of the material under test.

Instantaneous values of modulus representing the ratio between stress and strain of a viscoelastic material in an oscillation test is referred to as the materials "Complex modulus" (G*). This modulus is the sum of the elastic component (G') and the viscous component (G"). Therefore, knowing the value of G^* as well as the phase difference between (δ), G' and G" are given by:

$$G' = G^* \times Cos\ (\delta) \tag{3-2}$$

$$G'' = G^* \times Sin\ (\delta) \tag{3-3}$$

G' represents the recoverable energy in an elastic solid and is also called storage modulus. The energy lost due to permanent deformation in flow (i.e., viscous dissipation) is represented by G" that is also called loss modulus.

Parameters of oscillation test were measured at different frequencies ranging from 1 to 20 at constant strain of 10%.

3.4.3 Relaxation test

Stress relaxation is a technique for characterizing viscoelastic properties of polymeric systems. The test sample is subjected to a rapidly applied strain that is then held for the remainder of the test. The relaxation behavior is then studied by monitoring the steadily decreasing value of shear stress. For a pure Newtonian material, the stress will decay instantaneously whereas for a pure Hookean material there will be no decay. The simplest type of viscoelastic response is an exponential decay.

Basically relaxation modulus, G(t) representing stress/strain is measured during relaxation test that could also be interpreted as relaxation stress. The rate of stress relaxation (i.e., the intensity of relaxation process) is an important property of polymeric systems referred to as relaxation spectra, H(τ) that is defined by Eq. 3-4 (Alfrey and Doty 1945).

$$H(\theta) = -\left(\frac{dG(t)}{d\ln t}\right)_{t=\theta} \qquad 3\text{-}4$$

Where, θ is the relaxation time of the fluid. A constant strain of 10% was applied on the sample solutions during the rise time of 100 ms and stress relaxation was measured over 3 sec periods. In order to let the stresses induced during the placement of the sample be relaxed, the sample was rested for about 10 min before running the test. The result of both relaxation and oscillation tests are sensitive to the value of applied strain on the sample. Over straining the sample may destroy the elastic structure of the material and so it is important to keep the strain low. It is possible to continuously excite the sample without exceeding a level of strain, which would otherwise destroy the sample structure. Basically, for most of polymer melts and solutions oscillation test is in linear viscoelastic region if the amplitude is less than 10% (Walters 1975).

3.4.4 Creep test

Creep is defined as the slow deformation of a material, usually measured under a constant stress. During a creep test, a small stress is applied on the sample and the resultant strain is measured while the stress is held constant. The response of a viscoelastic material under creep test is initially provided by elastic components followed shortly by viscoelastic effects. At sufficiently long time scales, the observed effects are only from the viscous components since the resultant strain is large enough to destroy the elastic structure of the material (see Fig. 3-5). The third case in Fig. 3-5 shows a typical curve produced by a viscoelastic material. The actual shape will be determined by the interaction of the viscous and elastic components.

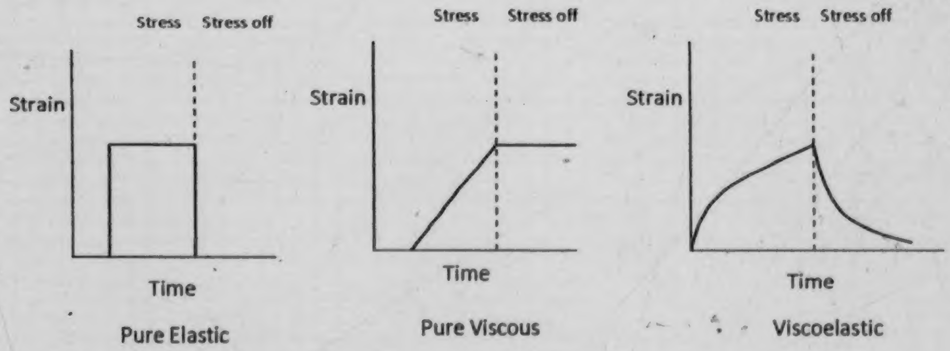

Fig. 3-5 Three different response curves in creep test

Since the actual change of strain will be dependent upon the applied stress, it is usual to report "compliance" rather than the strain. The compliance is defined simply as the ratio of the strain to the applied stress and is denoted by the letter *J (J=strain/stress)*. The creep test provides a method of determining the amount of elasticity in a sample. This value is denoted as Jo and is calculated by extrapolating back along the creep curve when in steady viscous flow. The intercept is then a measure of J_0 and since it is obtained from the creep test, it is recorded as Joc. This method is fine for estimating J_0 but it is prone to error since it generally involves extrapolating back from a large number to obtain a small number. J_0 could also be measured directly by the Creep-Recovery test (see Fig. 3-6). When steady viscous flow is reached, if the stress is removed, the material will recoil due only to the elasticity after waiting for at least as long as it took to obtain viscous flow (Bohlin Instruments, 1999). The measured recoil, or recoverable compliance is denoted by Jor. Generally Joc and Jor have the same order of magnitude but Jor is more accurate.

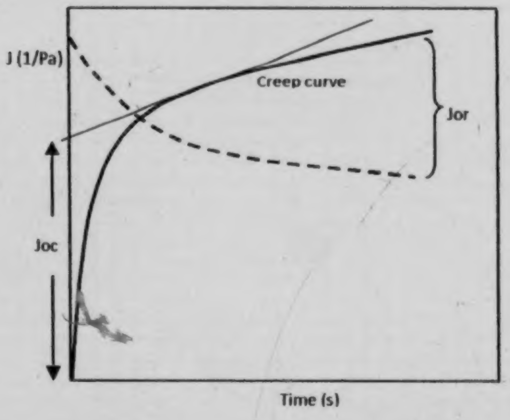

Fig. 3-6 calculating Joc and Jor using Creep and recovery curves

3.5 Core flow experiments

The core flow experiments were conducted in two different parts:

1. High permeability packing and High concentration solutions
2. Medium permeability packing and Medium concentration solutions

The absolute permeability of each packing was measured by water injection into the linear cell packed with the related glass bead. Polymer flow experiment was conducted in radial packing to simulate the more realistic wellbore geometry.

The experimental set-up and procedure used for core flow tests are described in the following sections.

3.5.1 Experimental set-up for core flow experiments

A schematic of the experimental set-up using radial and linear cells are shown in Fig. 3-7 and Fig. 3-8 respectively.

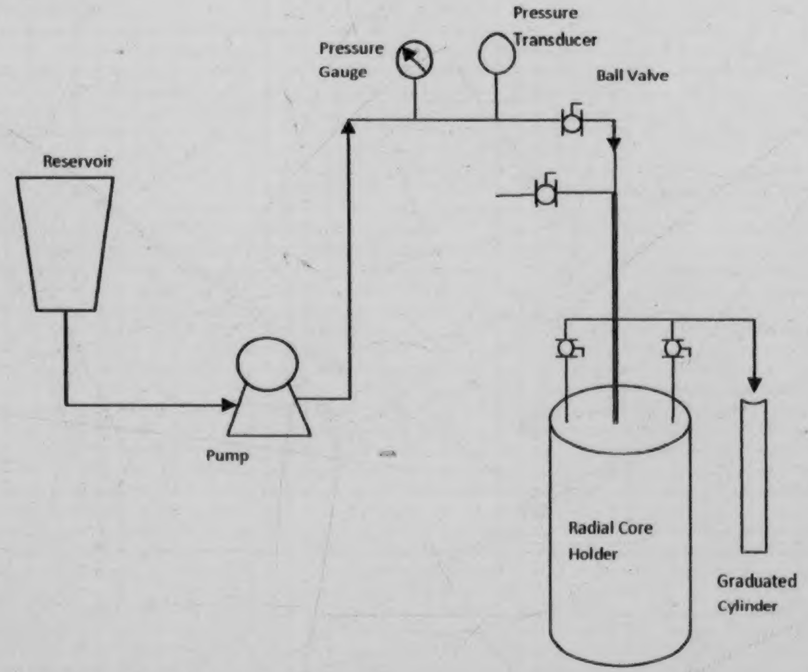
Pressure Transducer
Pressure Gauge
Ball Valve
Reservoir
Pump
Radial Core Holder
Graduated Cylinder

Fig. 3-7 Schematic of experimental setup of core flow experiment using the radial core holder

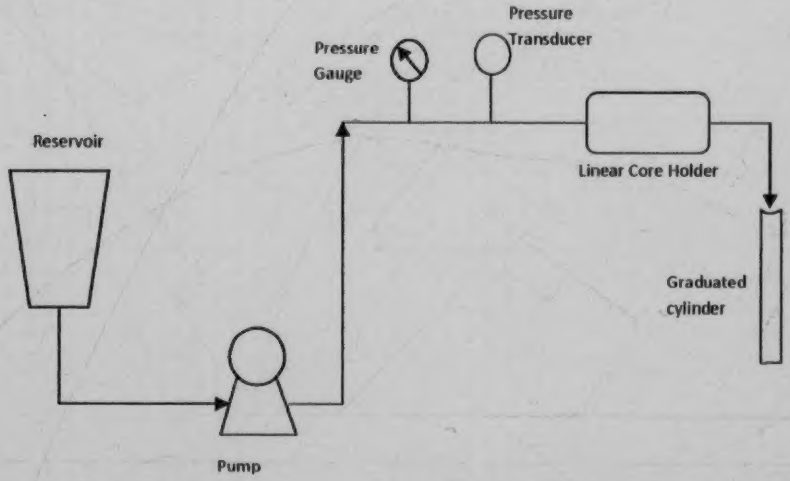
Pressure Transducer
Pressure Gauge
Reservoir
Linear Core Holder
Graduated cylinder
Pump

Fig. 3-8 Schematic of experimental setup of core flow experiment using the linear core holder

Different parts of the experimental set-up are explained in the following section.

Pump

A progressive cavity pump with variable frequency drive control was used to inject test fluid into the core sample (see Fig. 3-9).

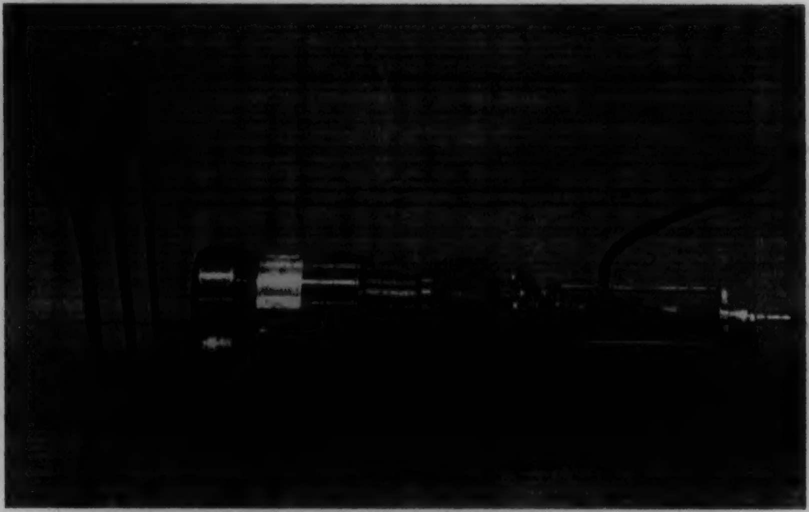

Fig. 3-9 Positive displacement pump used to inject water and polymer solutions

The frequency of the pump could be changed from 0% to 100%. Each value between 0 and 100 corresponds to a specific flow rate according the calibration curve shown in Fig. 3-10.

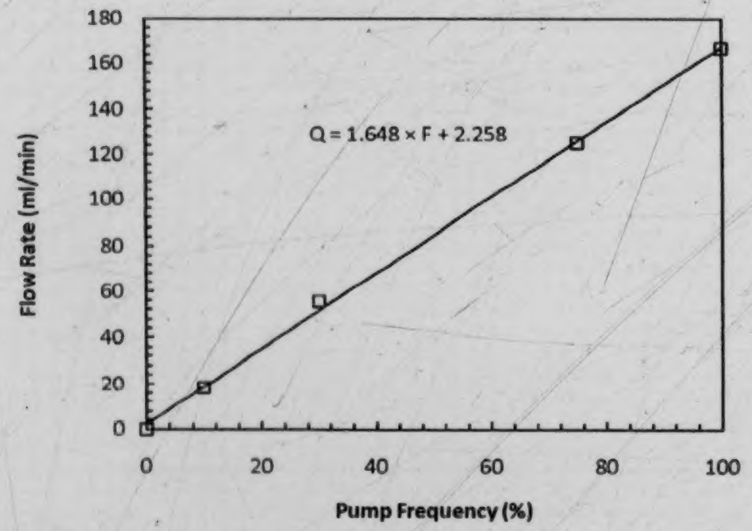

Fig. 3-10 Calibration curve for pump flow rate

Pressure gauge

Two different pressure gauges were used in these experiments.

1- Digital pressure gauge with the range of 0 to 30 psi and resolution of 0.01 psi. This high resolution pressure gauge was used to measure pressure drop of water in radial packing.
2- Analogue gauge with the range of 0 to 300 psi and resolution of 1 psi.

Data Acquisition System

The data acquisition system used had two parts: hardware and software systems. The hardware consisted of a transducer and OWL Data Logger. OWL Data Loggers record readings continuously at a fixed sample interval. Using an optical link, it transfers these readings to an IBM PC or 100% compatible computer for analysis with ACR's TrendReader software.

The pressure data were recorded every 8 seconds. Trend Reader software transferred the recorded data to pressure values in psi using a linear calibration. Very high and very low values of pressure data were filtered out and the mean value was recorded as the injection pressure of each flow rate.

Radial Cell

In order to simulate the actual wellbore conditions, a core holder with the following specifications was designed to ensure radial flow. The core holder consists of an injection line located in the middle of pressure vessel and two production line located in the boundaries of the vessel.

Fig. 3-11 shows the relative position of injection and production lines on the radial cell. Both the injection and production lines are encased by a screen. The opening of the screen is around 10 micron and prevents glass bead production. Pressure rating of the chamber is 1200 psi.

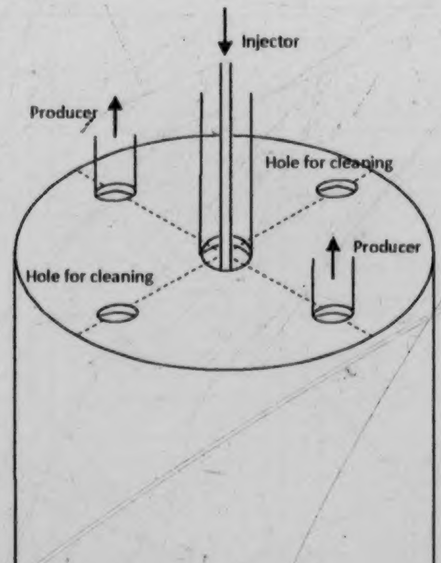

Fig. 3-11 Radial cell with one injector and two producer lines

A cross section of the radial cell showing the position of injector and producers is presented in Fig. 3-12.

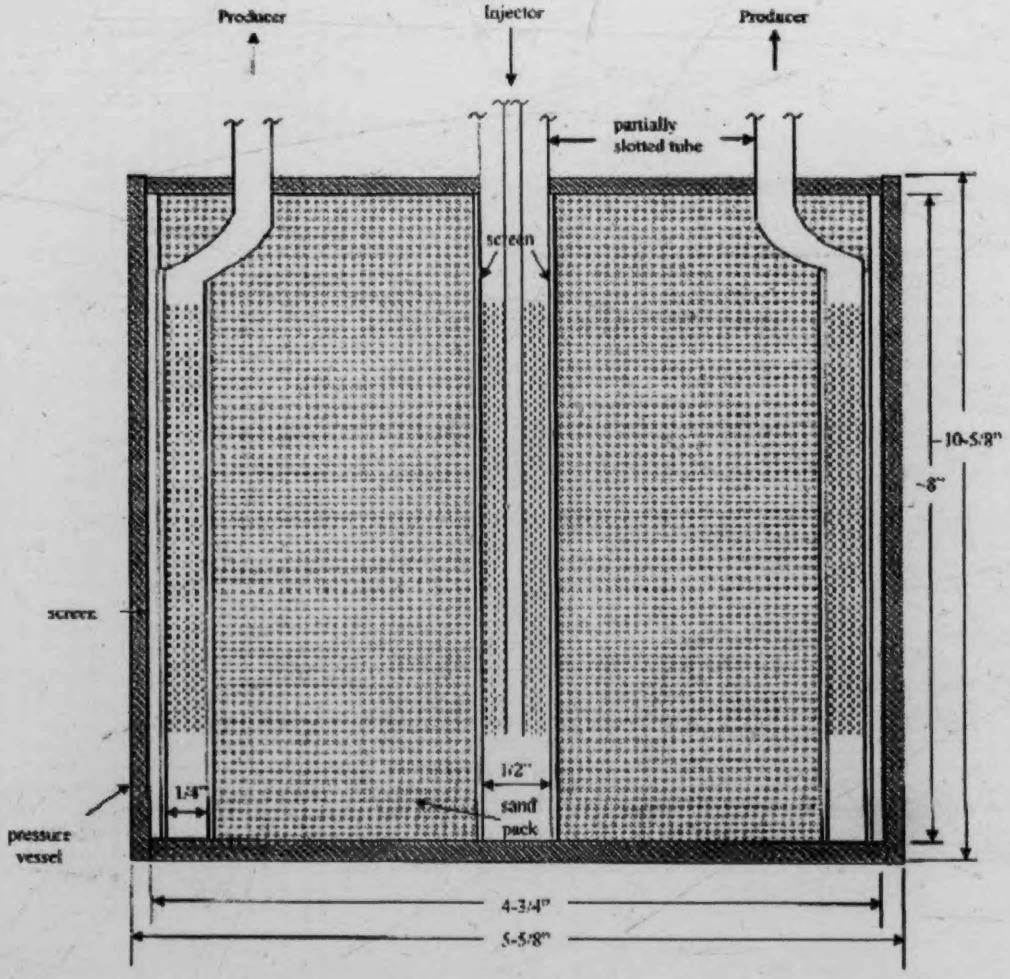
Producer
Injector
Producer
partially slotted tube
screen
10-5/8"
~8"
screen
pressure vessel
1/4"
1/2"
sand pack
4-3/4"
5-5/8"

Fig. 3-12 Cross section of the core holder showing the producing and injection lines

Injection line consists of an outer and inner tube. To prevent the wall effect, outer tube is slotted in the middle section of the inner tube. The sand pack inside the pressure vessel is encased by a screen. This screen ensures that the fluid produced is coming from entire outer surface of the packing. In other words, the screen to some extent prevents linear flow between the injector and producer and makes the assumption of radial flow more reasonable. The outer tube of the injection line is connected to a ball valve (see Fig. 3-13). During water injection the valve is open while the production lines are closed. This assures that the whole system is fully saturated with water and there is no air bubble trapped in the system. When water is produced from the outer tube of the production line, the relief valve is closed and production lines are open.

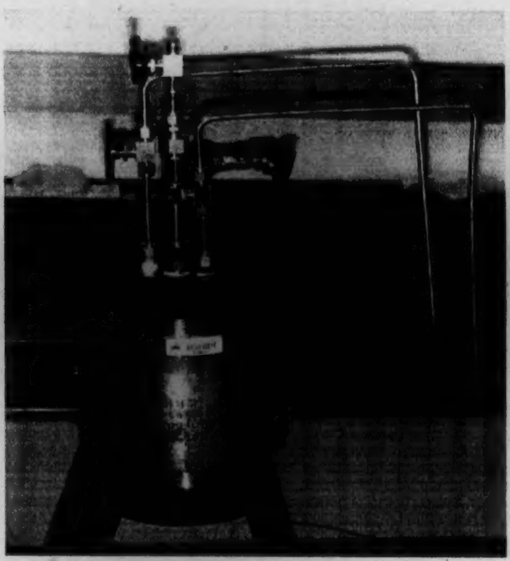

Fig. 3-13 Radial cell with injection and production lines

Linear Cell

In order to measure the packing permeability, a linear core holder was used. An 8-cm long and 2.5-cm diameter stainless steel core holder (Fig. 3-14) was used for linear core flow experiments. Two flanges were fitted on each end of the coreholder. A sintered screen was fitted into the inside wall of the cap flanges to act as a distributor for the fluids injected and also prevent glass bead production.

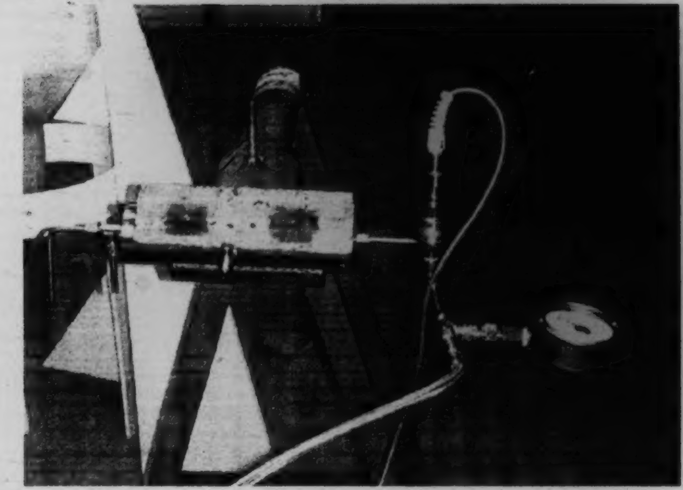

Fig. 3-14 Linear cell connected to pressure transducer and pressure gauge

3.5.2 Experimental Procedure

3.5.2.1 Packing Procedure

The core holder was packed with to two different glass bead grades. The size of glass beads used for high and low permeability packing was 50-150 micron and 35 micron respectively. The glass beads were loaded into the coreholder while vibrating the cell. The vibration was provided by a mechanical vibrator that was strapped onto the core. The operation of the vibrator was based on the continuous movement of a steel ball inside the vibrator by air pressure. The core holder was also vibrated manually by using a plastic hammer. The glass bead loading was continued until the time that no more space is provided by further vibration.

3.5.2.2 Core flow experiment procedure

In order to simulate the actual field condition during drilling, radial cell was used for polymer flooding experiment. However, the actual flow regime may not be purely radial in the radial packing. Therefore, linear cell was used to measure the absolute permeability of the packing by injecting tap water.

3.5.2.2.1 Permeability measurement using linear cell

The core holder was put in a horizontal position for absolute permeability measurement. The core initially was 100% water saturated and the pressure inside the core pack was atmospheric. Tap water was injected at different flow rates from the inlet and produced at the outlet end of the core. The pressure drop during water injection into the high permeability packing was relatively low. Therefore, digital pressure transducer with the resolution of 0.01 psi was used to measure the pressure drop. Stabilized pressure data corresponding to each flow rate was recorded. Darcy's law for linear flow was used to calculate the absolute permeability for each experiment.

3.5.2.2.2 Polymer flooding in radial cell

After preparing each sample solution and packing the core holder with glass beads, polymer injection was conducted through the following steps.

1- Water injection

Before injecting the polymer solution into the system, water was pumped at different flow rates to investigate the flow performance of water in the system. During water injection into the dry packing, production lines were closed. After producing water from the horizontal line connected to the outer tube of injection line, relief valve was closed and production lines were open. Water was injected into the system at different flow rates by setting the pump frequency. The stabilized pressure at each flow rate was recorded using digital pressure gauge.

2- Water displacement by polymer solution

Required volume of the sample solution (About 3 times of the pore volume) was injected into the porous media to displace the water. The viscosity of each sample polyox solution was relatively high. Therefore, water was easily displaced by viscous polymer. Polymer injection was continued until the stabilized pressure drop is obtained at a fixed flow rate. Finally, the viscosity of produced fluid was compared to the viscosity of polymer solution to make sure it is not contaminated with water.

3- Polymer solution injection

Polyox sample solution was injected at different flow rates into the radial core holder. 3 wt% solutions of polyox samples were injected into the high permeability system at flow rates ranging from 20 ml/min to 160 ml/min. Aqueous solutions of polyox samples with low concentration (1-1.5 wt%) were injected into the low permeability system at flow rates ranging from 6 ml/min to 100 ml/min. At each flow rate, the injection was continued until the pressure drop stabilized. The viscosity of produced polymer was measured to investigate shear degradation and polymer adsorption/entrapment in porous media.

4- Polymer solution displacement by water

After the flow test the core was flushed with water to clean the core out of polymer solutions. Water injection was continued until the pressure drop was stabilized. The viscosity of produced water was checked to make sure that produced water is not contaminated with polymer. However, some polymer might have remained in the system due to adsorption/entrapment in porous media.

5- Water back flush

During core flow experiment in the radial system, small glass bead particles create a filter cake at the outer surface of the production lines. This filter cake generates additional pressure drop due to skin effect. Water was injected from production lines while being produced from the injection line. Water back flush gradually removes the glass bead cake around the production line.

6- Water injection

The permeability of the core pack was measured after polymer solution displacement by water. In order to measure the flushed permeability, water was injected into the system at different flow rates. Difference in the permeability before and after the core flow tests were taken as the formation damage induced due to polymer solution flow.

CHAPTER 4

EXPERIMENTAL RESULTS AND DISCUSSION (RHEOLOGY)

In this chapter the effect of average molecular weight on rheological behavior of aqueous solutions of polyox grades is investigated. Average molecular weight and shear viscosity of polyox blends, predicted by suggested new mixing rule, is compared with experimental data. The effect of molecular weight distribution on viscoelastic behavior of polyox blends with similar shear viscosity (i.e., similar average molecular weight) is also investigated.

4.1 Rheological characterization of monodisperse polyox solutions

In this section the effect of average molecular weight on rheological properties of four different polyox grades with narrow MWD is investigated.

4.1.1 Viscometry tests

Aqueous solutions of 4 different polyox grades with different average molecular weights were characterized by viscometry test. Shear viscosity and normal force of these solutions are compared in Fig. 4-1and Fig. 4-2 respectively.

Basically all samples present similar shear thinning behavior but the value of μ_0 strongly depends on the average molecular weight. However, at high shear rates, the values of shear viscosity are close to each other due to shear thinning behavior of the solutions.

Both shear viscosity and normal stress considerably increase with increasing the molecular weight. Shear thinning behavior is more pronounced in case of polyox grades with higher average molecular weight. The effect of average molecular weight on shear behavior (i.e., shear viscosity and normal stress) of polyox grades is more pronounced at low shear rates.

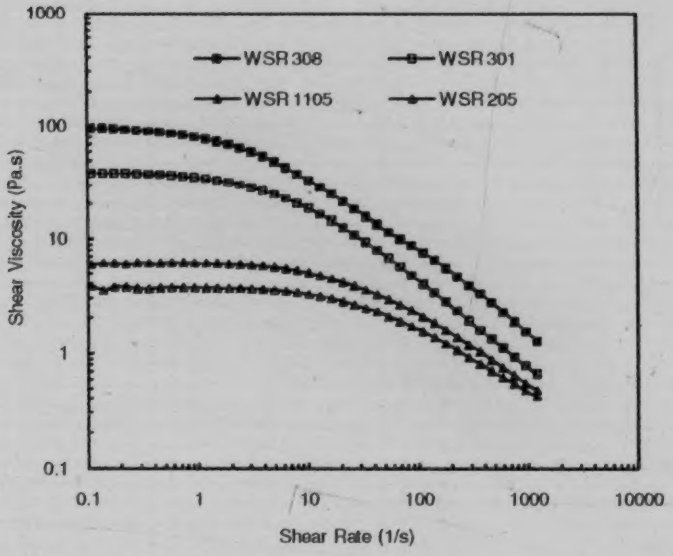

Fig. 4-1 Shear Viscosity vs. shear rate of aqueous solutions of different polyox grades (5 wt. %)

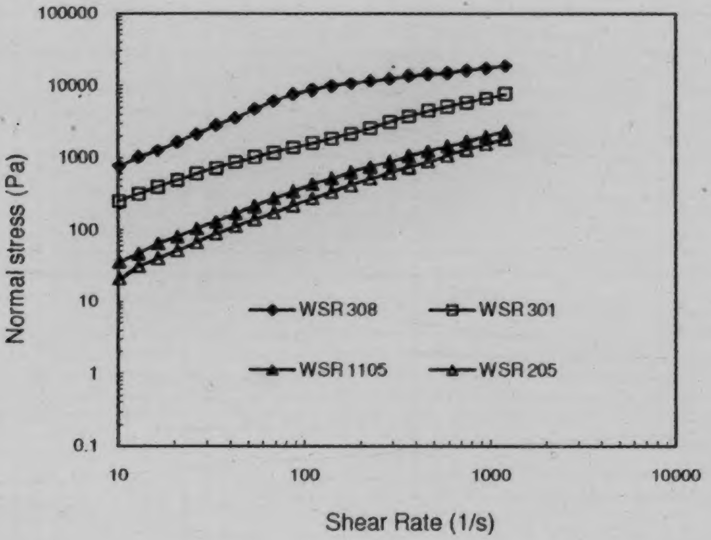

Fig. 4-2 Normal stress vs. shear rate of aqueous solutions of different polyox grades (5 wt. %)

4.1.1 Oscillation tests

Average molecular weight of polyox grades strongly influences parameters of oscillation test. Fig. 4-3 and Fig. 4-4 show the effect of molecular weight on elastic and viscous modulus of four different polyox grades respectively. Modulus values of polyox solutions considerably increase as the average molecular weight of the polyox grades increases. it is also observed that both elastic and viscous modulus values increase with increasing the frequency of the oscillation test.

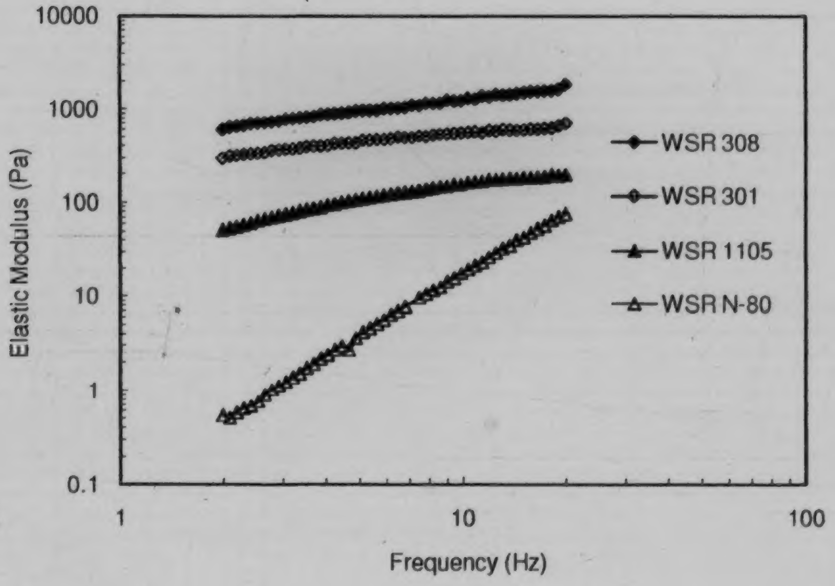

Fig. 4-3 Elastic modulus-frequency profile of aqueous solutions of 4 different polyox grades (6 wt. %)

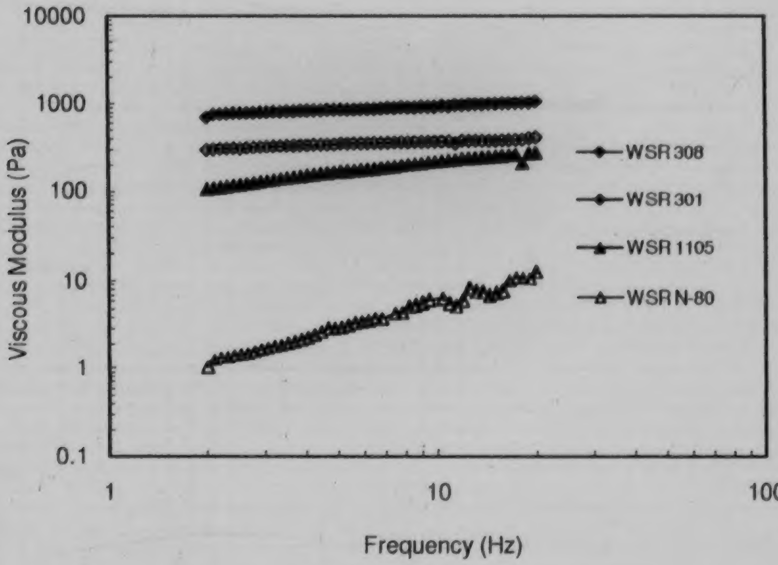

Fig. 4-4 Viscous modulus-frequency profile of aqueous solutions of 4 different polyox grades (6 wt. %)

4.2 Rheological characterization of polydisperse polyox solutions

4.2.1 Mixing Rule

Zero shear viscosity, μ_0, could be considered as an intrinsic property of each polymeric liquid that is related to average molecular weight according to the Eq. 2-14.

Fig. 4-5 shows measured values of μ_0 as a linear function of M_w for different grades of Polyox in logarithmic coordinate. This linear profile is in good agreement with Eq. 2-14 with the value of a being about 1.264. It is revealed from Fig. 4-5 that the molecular weight of the polyox grades is higher than critical molecular weight (M_c) of this polymer (Graessley, 1974). Different blends of Polyox with similar average molecular weight are expected to have approximately identical values of μ_0.

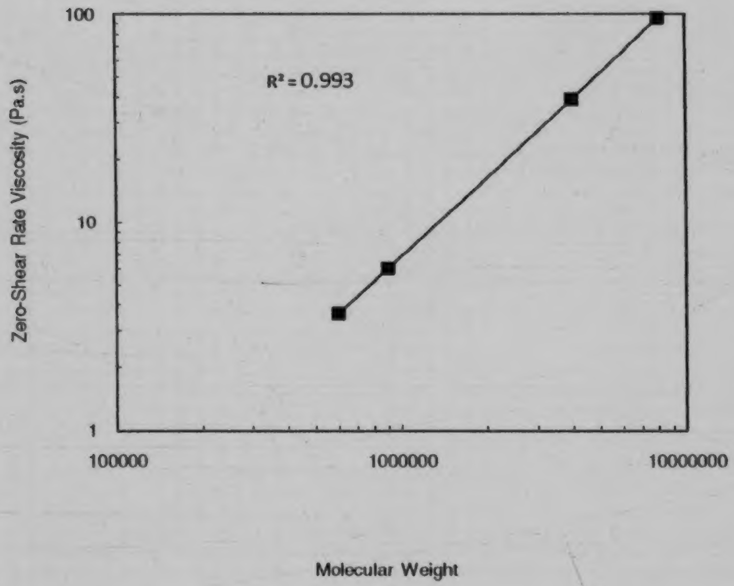

Fig. 4-5 Zero-shear rate viscosity versus molecular weight for 5 wt % aqueous solution of Polyox

Weight average M_w of each blend may be approximately calculated according to the following expression (Zang et al. 1987):

$$M_{w,B} = \sum_{i=1}^{n} \omega_i M_{w,i} \tag{4-1}$$

Here ω_i is the weight fraction of polymer i and B denotes the blend that is composed of n different polymer grades. Combining Eq 4-1 and Eq. 2-14 the following expression is given for zero-shear rate viscosity of polymer blends (Struglinski and Graessley 1985).

$$\mu_{0,B} = (\sum_{i=1}^{n} \omega_i \mu_{0,i}^{1/a})^a \tag{4-2}$$

In order to prepare mixtures of similar M_w and varying molar mass distribution, monodisperse Polyox grades were blended. 5 wt % aqueous solutions of different blends of Polyox with varying mixing ratio were prepared (Table 4-1).

Table 4-1 Polydispersity factor and composition of different Polyox Blends

Blend	Blend Composition (wt. %)				Mw/Mn (Eq.4-6)	$M_w/10^6$ (Eq.4-4)
	WSR 308	WSR 301	WSR 1105	WSR 205		
1	47	0	0	53	3.84	2
2	37	0	63	0	2.63	2
3	20	32	22	26	2.53	2
4	0	60	0	40	2.16	1.9
5	0	50	35	15	1.84	1.8
6	20	0	0	80	2.83	1
7	0	20	0	80	1.77	0.9
8	20	40	40	0	2.03	2.5
9	40	30	30	0	2.14	3.4
10	40	50	10	0	1.51	4.5

Zero shear viscosity of aqueous solution of each mixture was measured. The linear profile shown in Fig. 4-5 was used to estimate the average molecular weight corresponding to measured shear viscosity related to each blend. This value was considered as measured molecular weight of aqueous solution of each blend.

A significant difference was observed between the measured M_w and μ_0 values of Polyox blends and the values predicted by Eq. 4-1 and Eq. 4-2 respectively (Fig. 4-6 and Fig. 4-7). It was seen that the Eq. 4-1 does not provide an accurate estimate of equivalent molecular weight of the Polyox mixtures, especially at high fraction of large macromolecules.

μ_0 and M_w are interrelated by a power law relationship. The correlation coefficients a and K depend on the type of polymer and the temperature of the system. Both a and K are independent of μ_0 and M_w for monodisperse polymers. Therefore, the mixing rule giving the viscosity and molecular weight of polymer blends could also be assumed to be independent of these parameters. We suggested that mixture zero shear viscosity may be estimated by multiplying the viscosity of mixture components powered by their mass fraction. Eq. 4-3 is, therefore, proposed for calculating the equivalent mixture zero shear viscosity of aqueous solutions of polymer blends.

$$\mu_{0,B} = \prod_{i=1}^{n} \mu_{0,i}^{w_i} \qquad \text{4-3}$$

Fig. 4-7 shows that predicted values of μ_0 using Eq. 4-3 are reasonably close to measured values. Combining Eq. 2-14 and Eq. 4-3, the Eq. 4-4 is obtained for calculating the average molecular weight of a polymer blend.

$$M_{w,B} = \prod_{i=1}^{n} M_{w,i}^{w_i} \qquad \text{4-4}$$

As shown in Fig. 4-6, predicted values of M_w using Eq. 4-4 are in better agreement with the measured data than that of the ones predicted by Eq. 4-1.

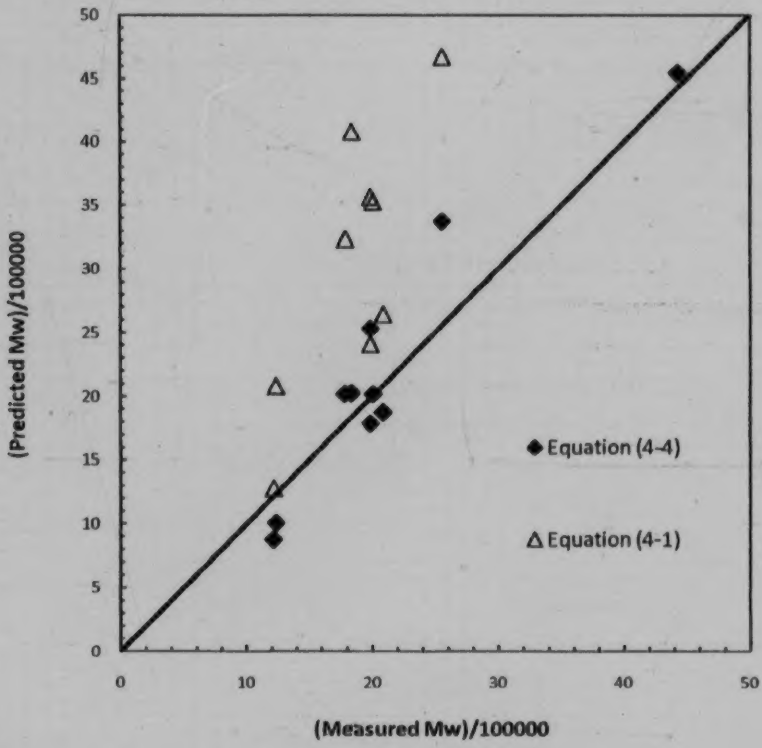

Fig. 4-6 Comparison of measured and predicted values of equivalent molecular weight of Polyox Blends (5 wt % aqueous solution)

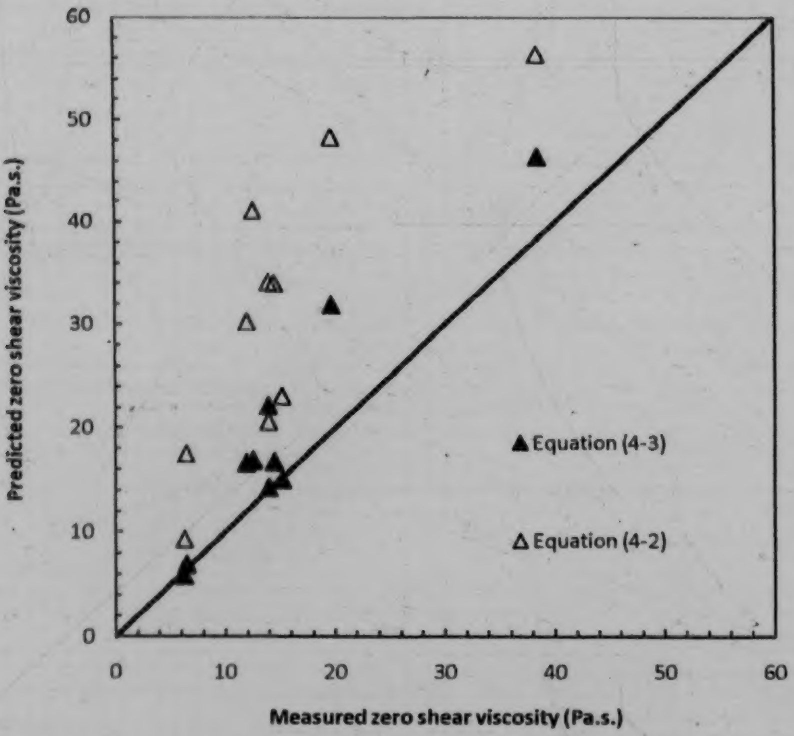

Fig. 4-7 Comparison of measured and predicted values of zero shear viscosity of Polyox blends (5 wt % aqueous solution)

4.2.2 Polydispersity

The effect of MWD on rheological properties of polymers is explained in the literature by considering polydispersity factors. Different models have been given for polydispersity factors of zero shear viscosity and recoverable compliance (Ressia et al. 2000). The value of Polydispersity defined by M_w/M_n could be measured by some experimental techniques. M_n is number average molecular weight that is defined by (Zang et al. 1987):

$$\frac{1}{M_{n,B}} = \sum_{i=1}^{n} w_i / M_{n,i} \qquad \text{4-5}$$

By assuming narrow molecular weight distribution for monodisperse samples, $M_{n,i}$ and $M_{w,i}$ may be considered identical. Therefore, approximate values of polydispersity of mixtures representing the broadness of molar mass distribution may be given by the following expression.

$$\frac{M_w}{M_n}=(\sum_{i=1}^{n}\omega_i M_{w,i})\times(\sum_{i=1}^{n}\frac{\omega_i}{M_{w,i}}) \qquad 4\text{-}6$$

Polydispersity values of different blends estimated by using Eq. 4-6 are given in Table 4-1.

4.2.3 Effect of MWD on shear viscosity of polyox blends

The first five blends listed in Table 4-1 have almost identical average molecular weight based on Eq. 4-4. Fig. 4-8 demonstrates the similar behavior of the blended samples in steady shear flow.

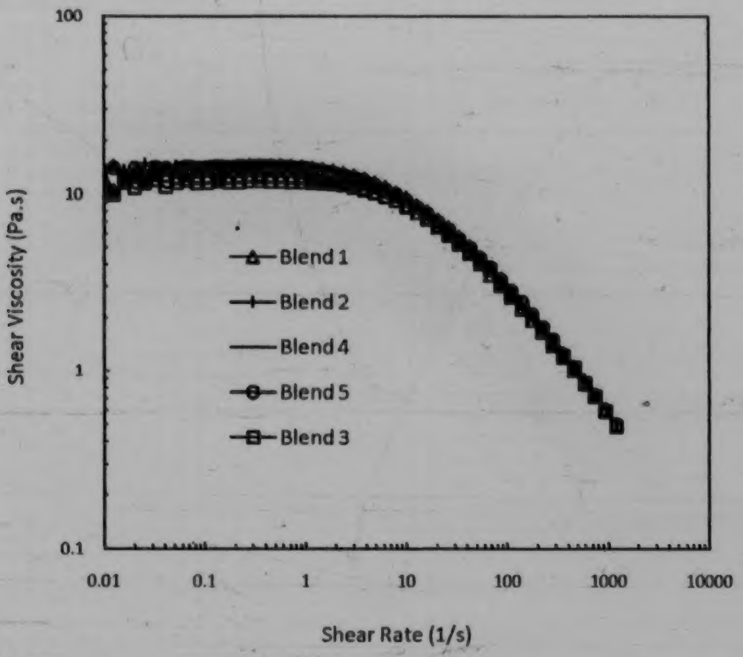

Fig. 4-8 Shear viscosity-shear rate profile of different polyox blends (5 wt%)

The effect of MWD and polydispersity on shear viscosity of polyox blends is negligible when the average molecular weight of blends is constant. Although there is a slight difference between zero shear viscosity of blends, they have almost identical shear viscosity at shear rates higher than 10 1/s. This is mainly due to similar shear thinning of the solutions.

4.2.4 Effect of MWD on the viscoelastic behavior of polyox blends

In order to prepare mixtures with similar shear flow behavior, blending ratio of each sample was selected based on proposed new mixing rule. In this section results on the rheological behavior of polyox blends with different molecular weight distribution, MWD, and similar average molecular weight, M_w is investigated. The effect of MWD and polydispersity on viscoelastic parameters obtained from transient rheological tests including relaxation, creep-recovery and oscillation tests are also analyzed.

If a sufficiently large strain (i.e., >10%) is applied, it is possible to break the elastic structure of a viscoelastic material, which would lead to purely viscous flow. Blended polyox samples with similar shear behavior (Fig. 4-8) may still show different viscoelastic behavior at low strain flow systems. However, the viscoelastic responses of these blends in relaxation and oscillation tests were difficult to be distinguished. In order to observe the effect of molar mass distribution of different polyox blends on the viscoelastic response of the aqueous solution of polyox blends, the following factors were considered:

- The concentration of solution was increased to have higher number of macromolecules in the test sample.
- Molar mass distribution (i.e., polydispersity value) of the samples was selected to be considerably different.

Aqueous solutions of two Polyox blends according to the mixing ratio listed in Table 4-2 were prepared at considerably high concentration of 10 wt%.

Table 4-2 Mixing ratio and approximate polydispersity value of two different Polyox blends

Sample	Weight Percentage			M_w/M_n Eq. 4-6	$M_w/10^6$ Eq. 4-4
	WSR N-80	WSR 1105	WSR 308		
Sample 1	0	100	0	1	0.9
Sample 2	25	50	25	4.6	1

4.2.4.1 Shear viscosity

Fig. 4-9 shows the similarity of shear flow characteristics of the solutions of two polymer blends, which have approximately equal values of average molecular weight.

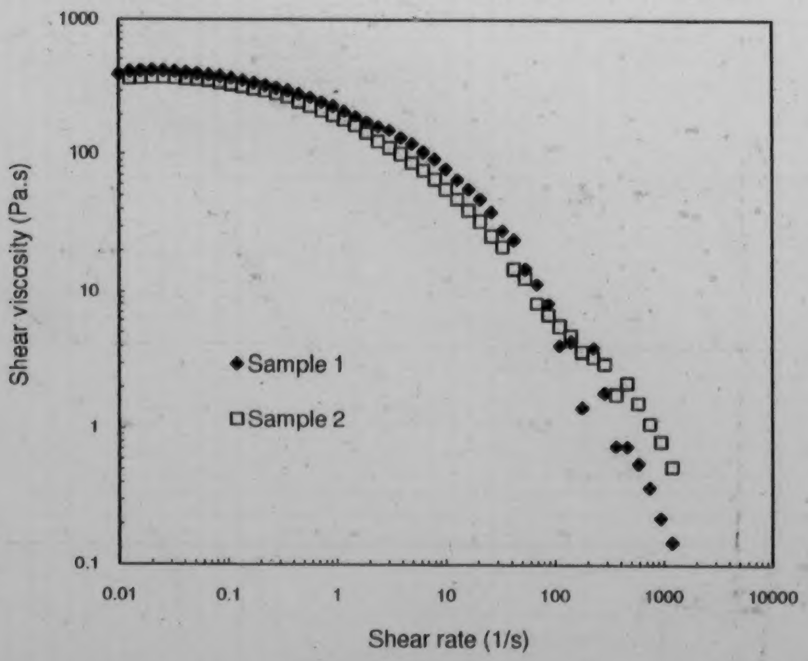

Fig. 4-9 Shear viscosity vs. shear rate of aqueous solutions of samples 1 and 2 (10 wt %)

While these two polymer blends have similar average molecular weight, they have significantly different polydispersity ratio. It is therefore, anticipated that solutions of these two polymer blends would show different viscoelastic characteristics. The following section presents the results of analyses of viscoelastic properties of the solutions of these two polymer blends.

4.2.4.2 Relaxation Test

Basically the result of relaxation test could be considered from two different points of view. The first one is relaxation modulus *G(t)* representing the rigidity and elasticity of the system. The second one is the rate of stress relaxation or the intensity of relaxation process indicating the flexibility of polymer molecules. The latter is reflected in relaxation spectra, *H(τ)* , that is defined by Eq. 3-4. Fig. 4-10 compares the relaxation modulus of the two samples as a function of time.

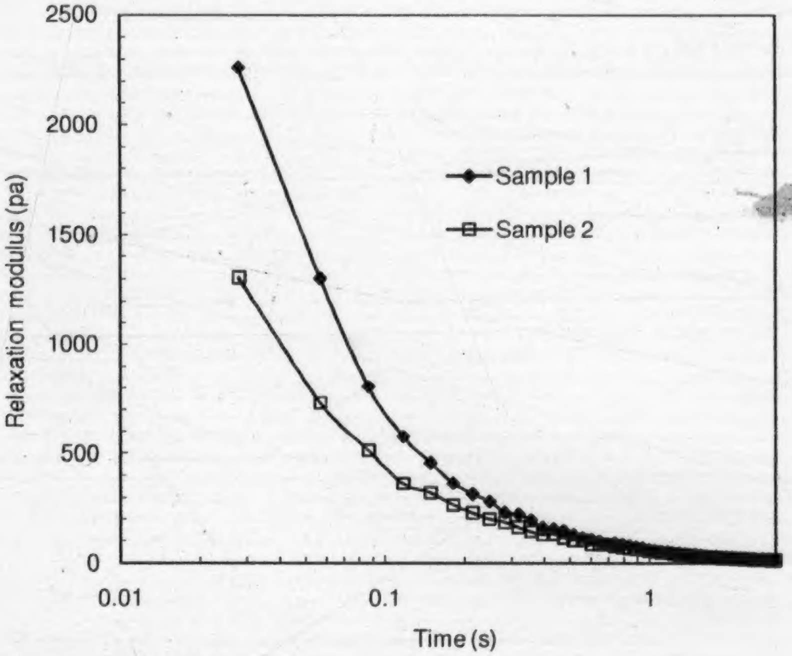

Fig. 4-10 Stress relaxation profile of aqueous solutions of samples 1-2 (10 wt %)

Fig. 4-10 shows higher values of *G(t)* of sample 1 (narrow MWD) compared to that of sample 2 (wide MWD). It is also seen that stress relaxation rate of the solution with narrow MWD is faster than that of the sample with broad molar mass distribution. The difference in relaxation rate may be due to presence of very large Polyox molecules

(WSR 308) in sample 2. For further investigation of relaxation process of the two solutions, their relaxation spectra was also compared (Fig. 4-11).

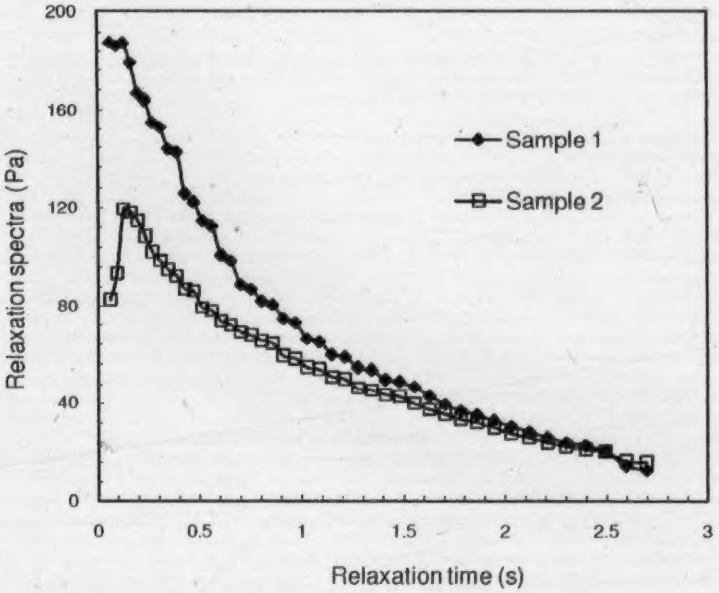

Fig. 4-11 Relaxation spectra of aqueous solutions of samples 1-2 (10 wt %)

As shown in Fig. 4-11, the relaxation spectra (i.e., intensity of relaxation process) is relatively higher in case of polyox solution with narrow MWD. This could also be explained by very large Polyox molecules (WSR 308) existing in sample 2. Such macromolecules slow down the relaxation process of the solution. The longest relaxation time also influences the flow behavior of polymeric liquids in low strain flow systems.Table 4-3 lists the values of dominant relaxation time (θ) and zero shear viscosity (μ_0) measured in relaxation test.

Table 4-3 Zero-shear rate viscosity and dominant relaxation time of aqueous solutions of samples 1 and 2 (10 wt %)

Blend	Dominant Relaxation Time (s)	Zero-Shear Rate viscosity (Pas)
Sample 1	0.127	226.41
Sample 2	0.197	178.97

Zero shear viscosity of sample with narrow MWD (sample 1) is higher than sample with wide MWD (sample 2) by 21%. Dominant relaxation time of sample with narrow MWD (sample 1) is 54% lower than sample with broad molar mass distribution. It may be concluded that sample solutions with wider MWD have less intense relaxation process and consequently higher values of the dominant relaxation time. These results are in agreement with the results of Plog et al. (2005) who reported relaxation time of polystyrene and methylhydroxyethyl blends measured by capillary break up experiment.

4.2.4.3 Creep-recovery test

Measured value of recoil denoted by Jor after removing the stress in creep test is representative of recoverable compliance due to only the elasticity of the system. The intercept of back extrapolating the creep curve is also reported by software (Joc) as a measure of recoverable compliance that is less accurate than Jor (see Fig. 3-6). Table 4-4 summarizes the result of creep and recovery test conducted on the two sample solutions.

Table 4-4 Summary of creep and recovery test results of aqueous solutions of samples 1and 2 (10 wt %)

Blend	J_{oc} (1/Pa)	J_{or} (1/Pa)	Mw /10^6
Sample 1	0.002	0.003	1.688
Sample 2	0.003	0.0044	1.563

Although average molecular weight of sample 1 measured in creep test is around 7 % higher than that of sample 2, the calculated values of J_{oc} and J_{or} for sample 1 are 50% and 48% lower than sample 2 with broader MWD, respectively. Higher values of J_{or} and J_{oc} could be interpreted as more dominant elastic properties. This result is in agreement with higher values of the longest relaxation time of sample 2. The presence of significantly large Polyox molecules contributes to higher flexibility and consequently larger deformation of sample 2 in creep test. Ressia et al. (2000) showed that a small fraction of high molecular weight polydimethylsiloxanes increased the recoverable compliance of monodisperse low molecular weight by about one order of magnitude. The results of both relaxation and creep-recovery tests show that sample with broad MWD (sample 2) behaves more elastically than sample with narrow MWD (sample 1) in low strain transient flow systems.

4.2.4.4 Oscillation Test

Frequency sweep test was conducted on the two solutions at constant strain of 10% that is assumed to be the maximum strain for linear viscoelastic response of polymer solutions. The result of oscillation test shows that both viscous and elastic modulus of sample 1 is higher than that of sample 2 (see Fig. 4-12 and Fig. 4-13). This could be explained by higher flexibility of sample 2 compared to sample 1.

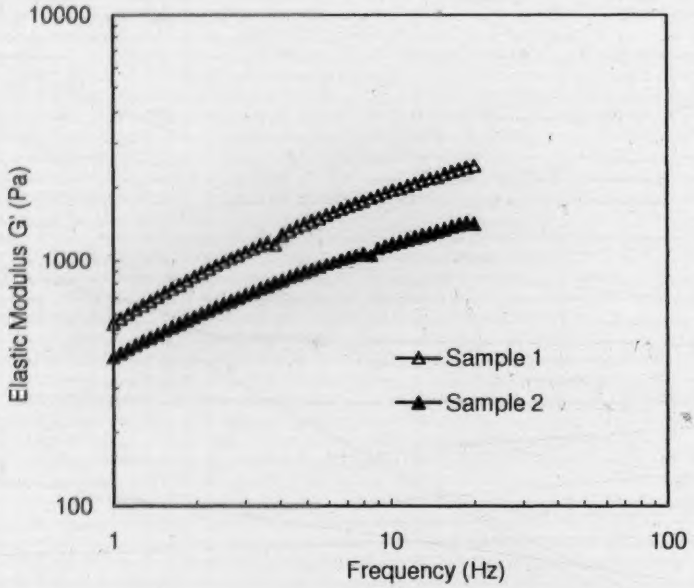

Fig. 4-12 Elastic modulus versus frequency of aqueous solutions of samples 1 and 2 (10 wt %)

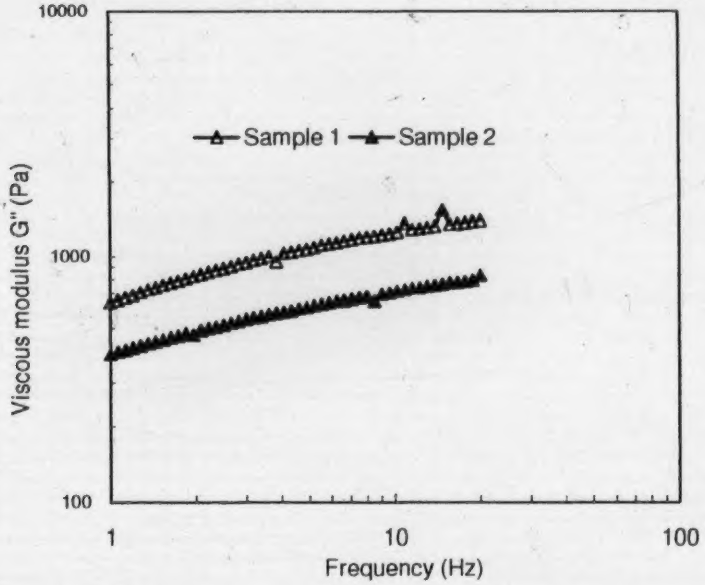

Fig. 4-13 Viscous modulus versus frequency of aqueous solutions of samples 1 and 2 (10 wt %)

Although a significant difference is observed between modulus values of the two samples, they presented similar viscous behavior (see Fig. 4-9). At high values of strain in simple shear flow, the structure of large polymer molecules (i.e., elastic part of a polymeric system) is broken. Therefore, samples 1 and 2 with different ratio of large Polyox molecules presented similar shear behavior. The G'/G" ratios indicating the relative elasticity of the two solutions are shown in Fig. 4-14. Again, results confirm that sample 2 is more elastic than sample 1.

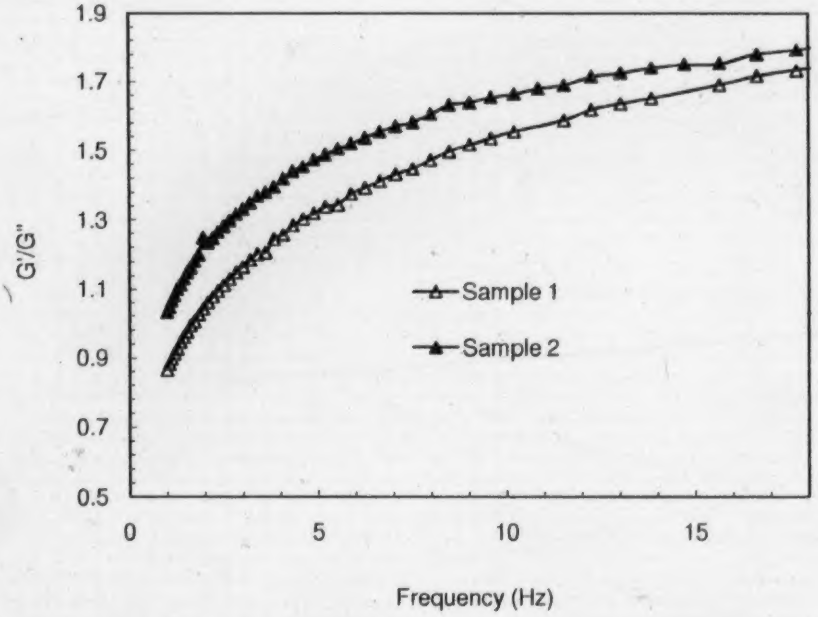

Fig. 4-14 G'/G" versus frequency of aqueous solutions of samples 1 and 2 (10 wt %)

4.2.4.5 Consistency between the results of oscillation and relaxation tests

In generalized Maxwell model (Ferry 1980), shear viscosity and elastic modulus of each element in a viscoelastic material is modeled by a dashpot and spring, respectively, that are in series with each other. Relaxation time of each element in Maxwell model is related to viscosity and elastic modulus by (Ferry 1980):

$$\theta_i = \mu_i / G_i \quad \text{4-7}$$

According to Eq. 4-7 considering polymer solutions with similar shear viscosity, those with lower values of elastic modulus are expected to have longer relaxation time. Basically, lower values of modulus could be interpreted as higher flexibility of a polymeric liquid that consequently results in longer relaxation time and less intense relaxation process. Therefore, the following expression is suggested for rough estimation of the ratio between relaxation time of the two Polyox blends with equal average molecular weight and shear viscosity.

$$\frac{\theta_{B1}}{\theta_{B2}} \approx \frac{G_{B2}}{G_{B1}} \tag{4-8}$$

Here, B denotes the blend and G is the general modulus (elastic, viscous or complex) value of the sample solution. Both the viscosity and modulus values of polymer solutions are function of shear rate, therefore, the initial conditions of the relaxation test could be considered to estimate the approximate value of maximum shear rate as follows:

$$\textit{shear rate} = \textit{initial strain/rise time} \tag{4-9}$$

Measured values of modulus (G', G'' and G^*) at frequency of about 1 Hz were used to estimate the ratio of G_{B2}/G_{B1} (see Table 4-5).

Table 4-5 Longest relaxation time and the result of oscillation test at frequency of 1Hz for aqueous solutions of samples 1 and 2 (10 wt %)

Sample	G' (pa)	G'' (pa)	G^*(pa)	θ(s)
1	553	638	844	0.13
2	391	404	562	0.2

The data listed in Table 4-6 shows that Eq. 4-8 provides a reasonable estimation for the ratio of relaxation time. It is also seen that the error would be less than 3% if complex modulus, G^*, is used in this expression.

Table 4-6 Measured values of parameters of Eq. 4-8 for aqueous solutions of samples 1-2 (10 wt %)

$\frac{\theta_{B1}}{\theta_{B2}}$	$\frac{G'_2}{G'_1}$	$\frac{G''_2}{G''_1}$	$\frac{G^*_2}{G^*_1}$
1.54	1.4	1.58	1.5

It was shown that relaxation time of polyox solutions could be increased at constant average molecular weight by increasing the broadness of molecular weight distribution. Measurement of dominant relaxation time of polymer solutions at low concentrations is relatively hard. Table 4-6 shows that the results of oscillation test could be used (Eq.4-8) for estimation of the ratio between relaxation time of two polymeric system with similar average molecular weight and different molecular weight distribution. This result is important for estimation of critical Deborah number and consequently critical flow rate related to flow of polymer solutions in porous media.

CHAPTER 5

EXPERIMENTAL RESULTS AND DISCUSSION (CORE FLOW EXPERIMENTS)

In this chapter, the results of core flow experiments are presented. Experiments are conducted by injecting two different polyox solutions through the radial cell packed with glass beads.

5.1 Absolute permeability measurement

Pressure drop of water was measured during flow in the linear cell packed with the two different sizes of glass beads. Darcy equation in linear systems was used to measure the absolute permeability:

$$\Delta P = \frac{\mu L}{K A} \times Q \tag{5-1}$$

Fig. 5-1 shows the profile of pressure drop versus water flow rate in linear cell packed with glass beads with average size of 75 micron (100-300 mesh).

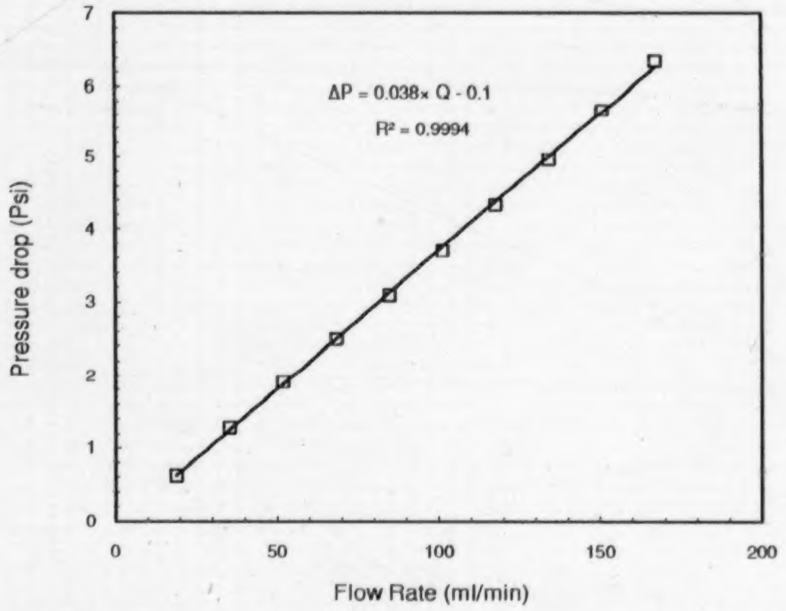

Fig. 5-1 Pressure drop vs. flow rate of water in the linear core (Media 1)

Using the slope of pressure drop-flow rate line (m), the absolute permeability is given by:

$$K = \frac{\mu L}{m A} = \frac{0.001\ (Pa.s)\times 7.56(cm)}{0.038\left(\frac{Psi}{ml/min}\right)\times 5.35cm^2} = 8.9\ Darcy \qquad 5\text{-}2$$

Linear core was also packed with glass beads with average particle diameter of 35 micron. The pressure drop of water was considerably higher than that of 100-300 mesh packing. Fig. 5-2 shows the linear profile of water pressure drop versus flow rate for this packing.

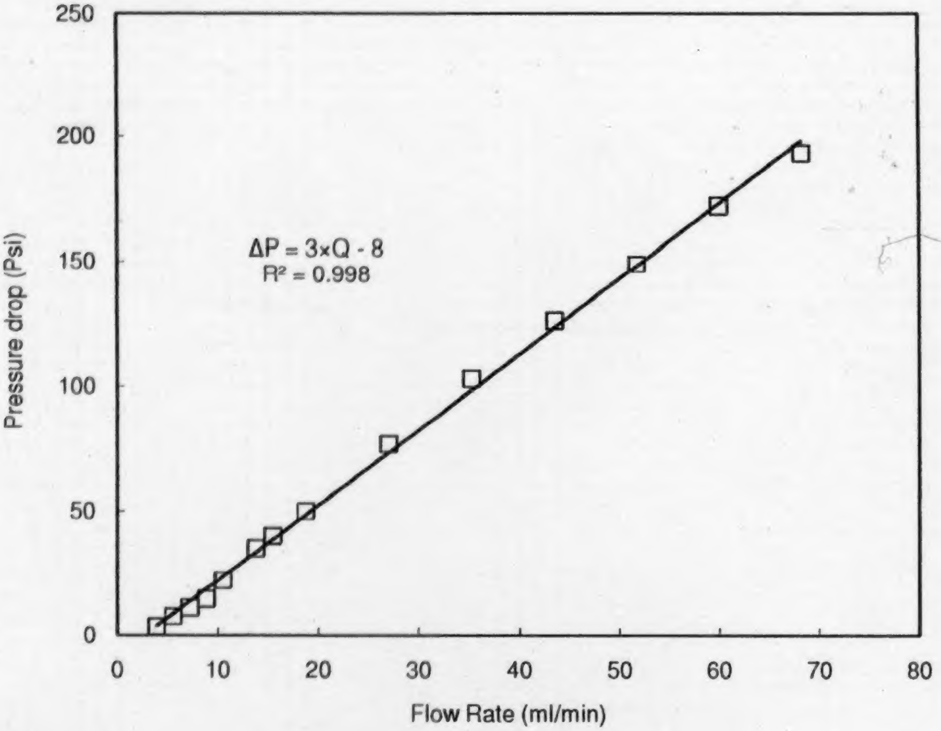

Fig. 5-2 Pressure drop vs. flow rate of water in the linear core (Media 2)

Similarly the absolute permeability is measured by using the slope of the linear profile and dimensions of the linear cell.

$$K = \frac{\mu L}{m A} = \frac{0.001\,(Pa.s) \times 7.56(cm)}{3\left(\frac{Psi}{ml/min}\right) \times 5.35cm^2} = 0.12\ Darcy = 120\ md \qquad 5\text{-}3$$

Table 5-1 summarizes the properties of the two porous media used in this study:

Table 5-1 Properties of the two different porous media used in core flow experiments

Porous media	Particle size	Permeability	Porosity
Media 1	75 micron (100-300 mesh)	8.9 Darcy	44%
Media 2	35 micron	0.12 Darcy	48%

5.2 Equivalent shear rate

Chauveteau (1982) suggested the equation 5-4 for determining average shear rate in porous media.

$$\dot{\gamma} = \frac{4\,\alpha\,q}{A\,(8k\varphi)^{0.5}} \tag{5-4}$$

α is the material constant that is 1.7 for glass beads. A is the cross sectional area that is calculated using the average diameter of the radial packing by:

$$A_{radial} = \pi \times \left(\frac{4.75+0.5}{2}\right) \times 8\ in^2 = 425.6\ cm^2 \tag{5-5}$$

Therefore, the following relationship is considered between the flow rate and equivalent deformation rate in radial cell:

$$\dot{\gamma}_{media\ 1}\left(\frac{1}{s}\right) = \frac{4\times 1.7}{425.6\ cm^2(8\times 8.9\ d\times 0.44)^{0.5}}\ q = 0.48\ q\ \left({}^{ml}/_{min}\right) \tag{5-6}$$

$$\dot{\gamma}_{media\ 2}\left(\frac{1}{s}\right) = \frac{4 \times 1.7}{425.6\ cm^2(8 \times 0.12\ d \times 0.48)^{0.5}}\ q = 3.9\ q\ \left({}^{ml}/_{min}\right) \tag{5-7}$$

At a constant flow rate, the equivalent shear rate in porous media 2 is around 8 times of shear rate in porous media 1.

5.3 Polyox solutions

Aqueous solutions of two different blends of polyox were prepared at different concentrations. The two blends had almost equal average molecular weight and different polydispersity values measured by Eq. 4-4 and Eq. 4-6 (see Table 5-2). Sample 2 with 25% mass fraction of WSR 308 grade and consequently higher values of polydispersity is anticipated to have higher elastic effects.

Table 5-2 Two different samples of polyox with similar average molecular weight and different polydispersity values

Polyox Blend	Weight Percentage			Mw/Mn Eq. 4-6	$Mw/10^6$ Eq. 4-4
	WSR N-80	WSR 1105	WSR 308		
Sample 1	0	100	0	1	0.9
Sample 2	25	50	25	4.6	1

5.4 Core flow experiments

The core flow experiments were conducted in two different parts. In the first group of the experiments radial cell was packed with 100-300 mesh glass bead (8.9 Darcy). 3 wt % aqueous solutions of samples 1 and 2 were injected into this media. In the second group of the experiments, the permeability of the system was reduced to 0.12 Darcy by packing the radial cell with 35 micron glass bead (media 2). The pressure drop of polyox solutions in porous media 2 was considerably higher than that of porous media 1. Therefore, the concentration of polyox solutions were reduced in the second group of experiments. 1 wt% aqueous solution of sample 2 and 1.25 wt %-1.5 wt % aqueous solutions of sample 1 were injected into this media.

5.4.1 High polymer concentration and high permeability experiments

Aqueous solutions of samples 1 and 2 with relatively high concentration of 3 wt % were injected in the radial cell packed with glass beads with average diameter of 75 micron (media 1). In the following sections the Rheological behavior and pressure drop of these two solutions in porous media is compared.

5.4.1.1 Rheological behavior of 3 wt% aqueous polyox solutions

- **Shear viscosity of polyox solutions**

The 3 wt% aqueous polyox solutions of samples 1 and 2 were characterized in viscometry test using Bohlin rheometer. Fig. 5-3 compares shear stress-shear rate profile of the two sample solutions.

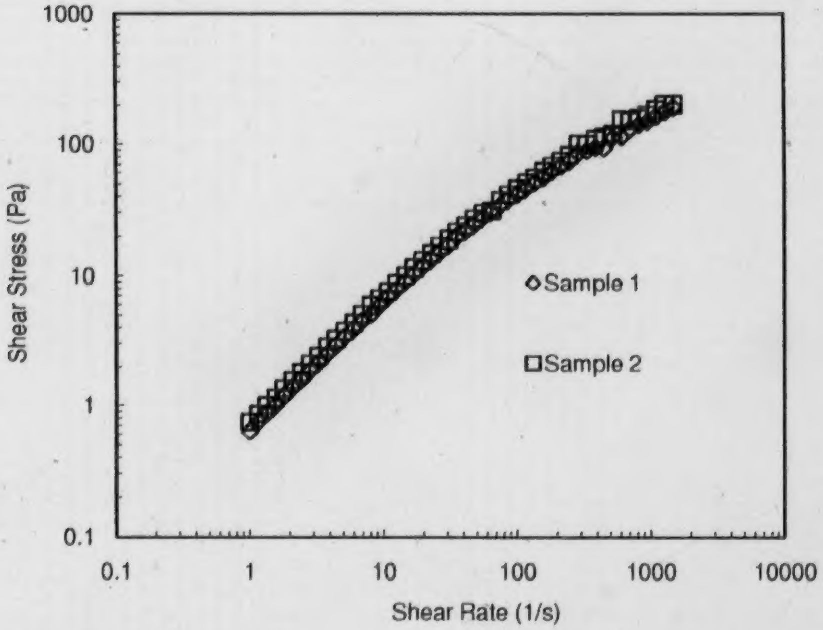

Fig. 5-3 Shear stress vs. shear rate of aqueous solutions of samples 1 and 2 (3 wt%)

As shown in Fig. 5-3, the two sample solutions have almost identical shear stress values. This is an expected behavior as the average molecular weights of the two samples are very close to each other. Shear thinning behavior of the solutions is also revealed in this Fig. 5-3. Both solutions have also identical values of shear viscosity. However zero shear viscosity of sample 2 is slightly higher than that of sample 1 (See Fig. 5-3).

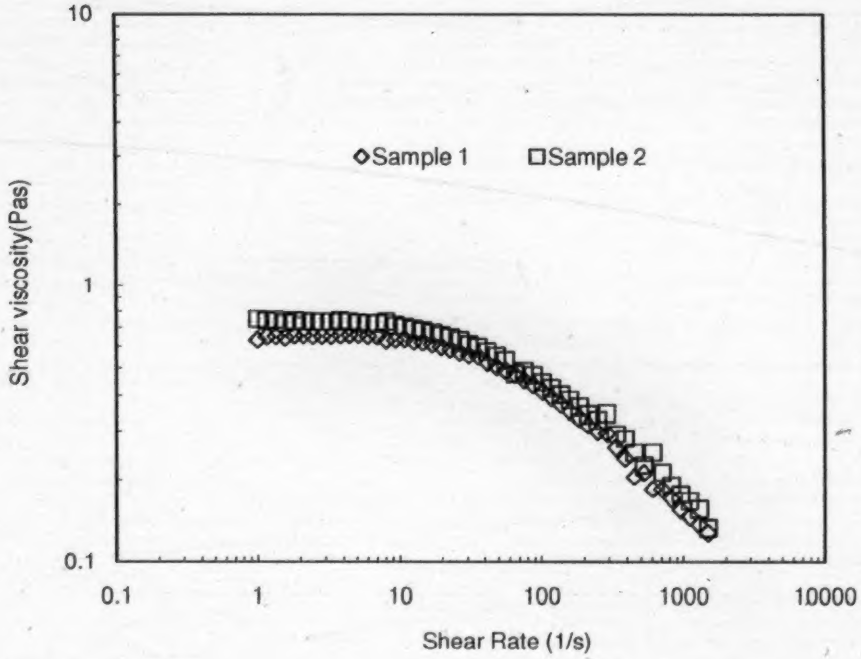

Fig. 5-4 Shear viscosity vs. shear rate of aqueous solutions of samples 1 and 2 (3 wt. %)

- **Normal stress of polyox solutions**

Although sample 1 and sample 2 presented similar viscous behavior (Fig. 5-3 and Fig. 5-4), normal stress values of the two solutions are significantly different (see Fig. 5-5). Sample 2 with higher values of normal force is anticipated to behave more elastically compared to sample 1.

Both shear stress and normal stress values increases with increasing shear rate. Normal force values of both solutions are higher than their shear stress values. Furthermore, the rate of increase of normal force values is faster than that of shear stress. It is anticipated elastic effects in addition to viscous forces may influence the flow behavior of the two solutions in porous media. Both solutions have similar shear viscosity, however, sample 2 has more elastic characteristics than that of sample 1. Therefore, it is expected that sample 2 show more resistance to flow in porous media than that of sample 1.

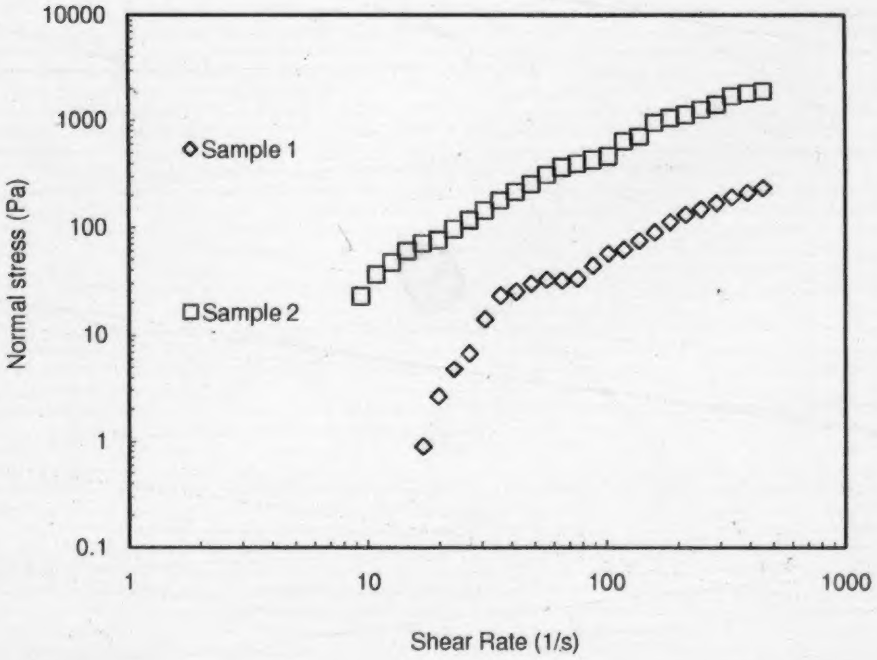

Fig. 5-5 First normal stress difference vs. shear rate of aqueous solutions of samples 1 and 2 (3 wt. %)

- **Extensional viscosity of polyox solutions**

Extensional viscosity of polymer solutions is representative of their elastic properties. In uniaxial elongational flow extensional viscosity is related to first normal stress difference by the following equation:

$$\mu_e = \frac{\tau_{11} - \tau_{22}}{\dot{\gamma}} = \frac{N_1}{\dot{\gamma}} \qquad 5\text{-}8$$

τ_{11} and τ_{22} are normal stress in the direction of flow and perpendicular to flow direction respectively. Higher values of first normal stress difference measured in simple shear flow can be considered as an indication of higher extensional viscosity. Therefore, it is expected that sample 2 with higher values of normal stress compared to sample 1, exhibit higher extensional viscosity during flow in porous media.

In addition to shear viscosity, extensional viscosity of polymeric systems with high values of normal stress may influence their flow performance in porous media. The higher the extensional viscosity, the more elastic will be the behavior of fluid in porous media. Trouton number representing the elastic effects of a polymeric liquid is defined by:

$$\text{⍰}r = \frac{\mu_e}{\mu} \qquad \text{5-9}$$

We also know that shear viscosity is defined by:

$$\mu = \frac{\tau}{\dot{\gamma}} \qquad \text{5-10}$$

Therefore, in uniaxial elongational flow systems Trouton value is given by:

$$\text{⍰}r = \frac{\mu_e}{\mu} = \frac{N_1}{\tau} \qquad \text{5-11}$$

The ratio of $\frac{N_1}{\tau}$ could be considered as an indication of extensional viscosity (i.e., elastic properties) of polymer solutions. Fig. 5-6 compares the value of $\frac{N_1}{\tau}$ of the two sample solutions. This dimensionless value can be considered as a good measure of elastic properties of a polymeric system.

Fig. 5-6 shows that elastic effects are more dominant in case of sample 2 compared to sample 1. The value of $\frac{N_1}{\tau}$ is less than 1 for sample 1 at shear rates less than 30 1/s. $\frac{N_1}{\tau}$ of sample 1 does not exceed 1 when shear rate is less than 100 1/s. It may be concluded that elastic behavior of sample 1 is negligible at shear rates lower than 100 1/s. While sample 2 is anticipated to have dominant elastic effects even at low shear rates.

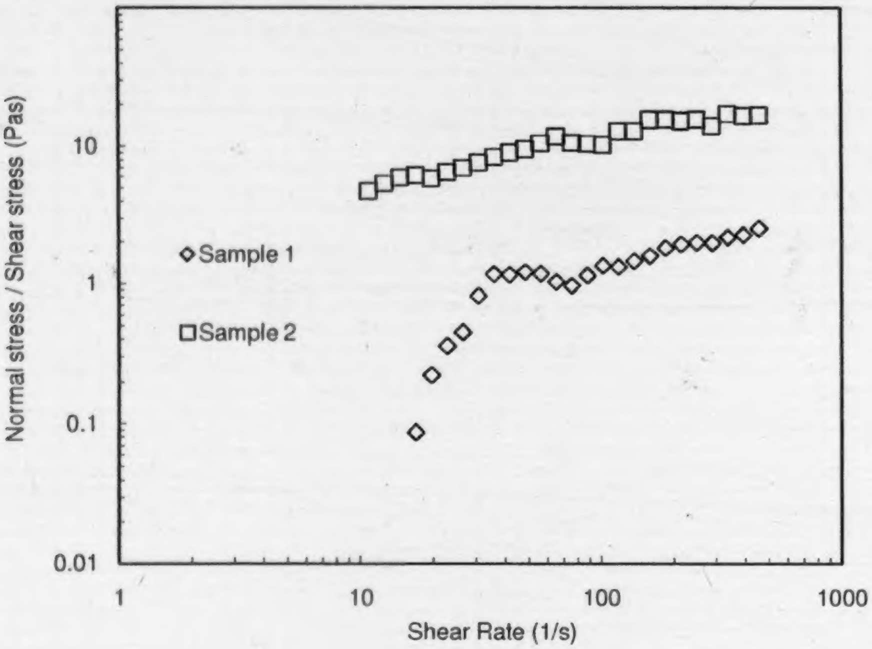

Fig. 5-6 The ratio between first normal stress difference and shear stress of aqueous solutions of samples 1 and 2 (3 wt. %)

- **Relaxation time**

According to Maxwell model relaxation time of a viscoelastic fluid is related to other rheological properties by Eq. 6-3. Calculated relaxation time vs. shear rate behavior of the two sample solutions is compared in Fig. 5-7. Relaxation time of sample 2 with broader MWD is higher than that of sample 1 with narrow MWD. These results are in agreement with the results of plog et al. (2005) that showed the influence of MWD on relaxation time of two different types of polymers measured by capillary break up technique.

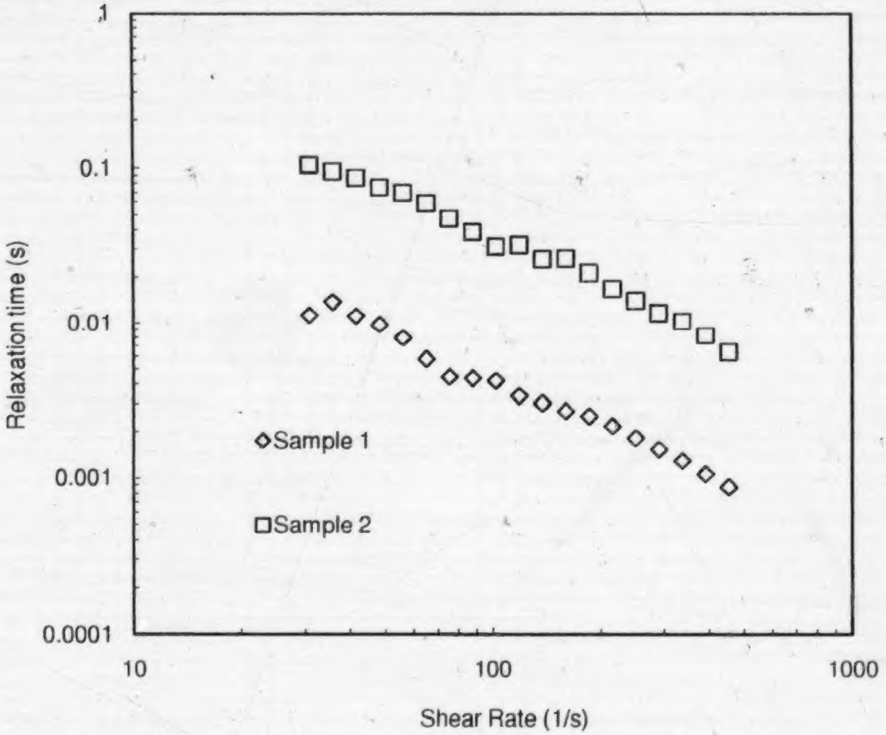

Fig. 5-7 Relaxation time vs. shear rate for aqueous solutions of samples 1 and 2 (3 wt %)

5.4.1.2 Pressure drop in radial cell

Flow tests were conducted in radial packing by injecting two different aqueous solutions of polyox (Samples 1 and 2 in Table 5-2). Stabilized value of pressure drop at each flow rate was recorded. Fig. 6-2 compares pressure drop of the two sample solutions at different flow rates.

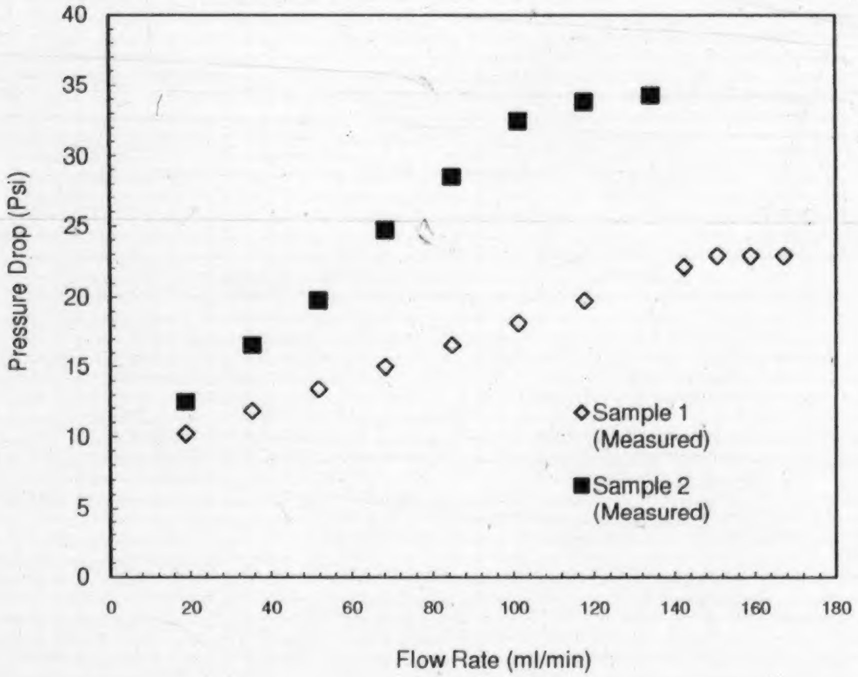

Fig. 5-8 Pressure drop-flow rate for aqueous solutions of sample 1 and 2 (3 wt %)

At high flow rates, shear thinning of the solutions is observed as shown in Fig. 5-8. Pressure values and the rate of pressure increase with flow rate are considerably higher in the case sample 2. The shear viscosities of the two solutions were almost identical. It was shown that normal stress values of sample 2 were considerably higher than that of sample 1. The values of $\frac{N_1}{\tau}$ and relaxation time of sample 2 were considerably higher than that of sample 1 (see Fig. 5-6 and Fig. 5-7). Therefore, some of the additional pressure drop due to the flow of sample 2 can be contributed to its elastic properties. Furthermore, sample 2 with broader molecular weight distribution may have higher values of extensional viscosity. It has been shown in literature that Polystyrene and MHEC blends with broader molar mass distribution have higher values of extensional viscosity and relaxation time measured by capillary breakup technique.

The two sample solutions are sheared and elongated during their flow through porous media. But the resistance of sample 2 against extensional forces is higher as its normal force values are higher than that of sample 1. This consequently results in higher pressure drop of sample 2.

It is also shown in Fig. 5-8 that pressure drop-flow rate behavior of the two solutions indicates two different regions:

1. Linear behavior (low and medium flow rates)
2. Shear thinning behavior (High flow rates)

5.4.2 Low polymer concentration and low permeability experiments

1.25 wt % and 1.5 wt % aqueous solutions of samples 1 and 1 wt % aqueous solution of sample 2 were injected in the radial cell packed with 35 micron glass beads (media 2). In the following sections the rheological behavior of these two solutions and the pressure drop due to flow of these two solutions through porous media are discussed.

5.4.2.1 Comparison of rheological behaviors of sample 1 (1.25 wt %) and sample 2 (1 wt %)

Shear viscosity of 1 wt% aqueous solution of sample 1 was relatively lower than that of 1 wt% sample solution 2. Shear viscosity of 1.25 wt% aqueous solution of sample 1 was very close to that of 1 wt % solution of sample 2. Therefore, flow performances of these two solutions were compared to investigate potential influence of elastic properties on pressure drop in porous media.

- **Shear viscosity**

Fig. 5-9 shows that shear stress of the two solutions measured in simple shear flow (i.e., viscometry test) are almost identical at different shear rates. It is anticipated that viscous forces similarly affect the flow performance of these two solutions in porous media.

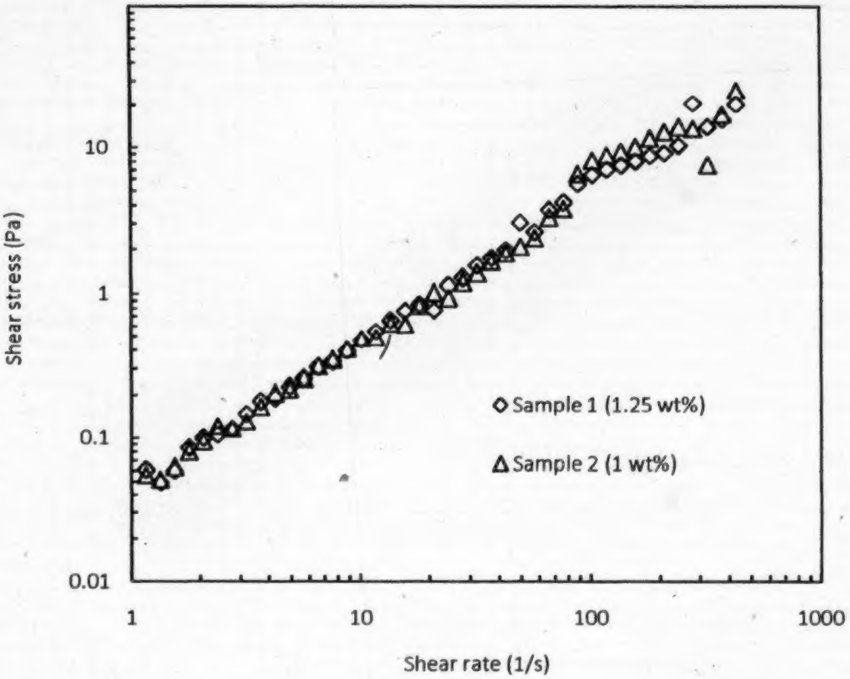

Fig. 5-9 Shear stress versus shear rate for aqueous solutions of sample 1 (1.25 wt %) and sample 2 (1 wt %)

Fig. 5-10 shows that the shear viscosities of the two solutions are almost identical. Although 3 wt % aqueous solutions of samples 1 and 2 presented very strong shear thinning behavior (see Fig. 5-4), the viscosities of the two solutions at low concentrations weekly depend on shear rate (see Fig. 5-10).

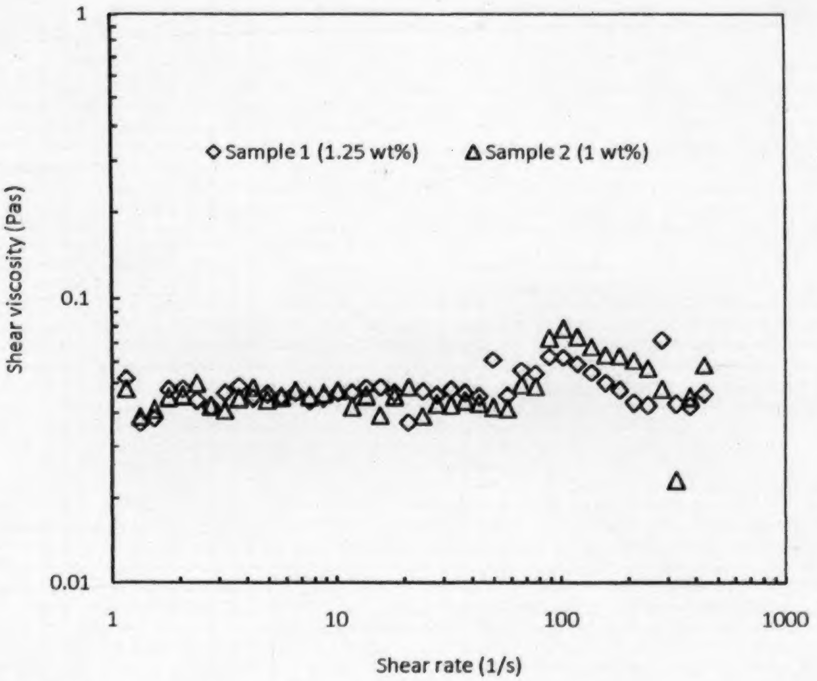

Fig. 5-10 Shear viscosity versus shear rate for aqueous solutions of sample 1 (1.25 wt %) and sample 2 (1 wt %)

- **Normal stress**

Normal and shear stresses of the two sample solutions were measured simultaneously in viscometry test. Fig. 5-11 shows that there is a significant difference between normal stress values of the two solutions. However, shear stress values of the two solutions were almost identical (see Fig. 5-9).

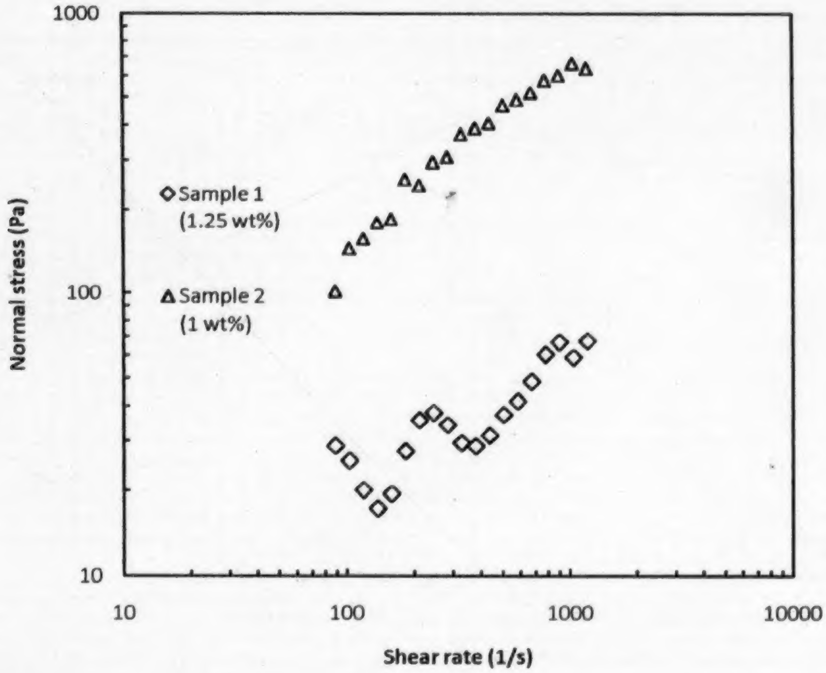

Fig. 5-11 Normal stress versus shear rate for aqueous solutions of sample 1 (1.25 wt %) and sample 2 (1 wt %)

Although viscous behavior of the two solutions is very similar, elastic properties of sample 2 (1 wt %) are anticipated to be significantly higher than that of sample 1 (1.25 wt %).

Fig. 5-12 compares the values $\mathbf{N_1/\tau}$ for the two solutions. It may be concluded from these data that extensional viscosity of sample 2 (1 wt %) is approximately one order of magnitude higher than that of sample 1 (1.25 wt %). Therefore, in flow systems with extensional deformation, sample 2 with higher values of $\mathbf{N_1/\tau}$ may experience higher resistance compared to sample 1.

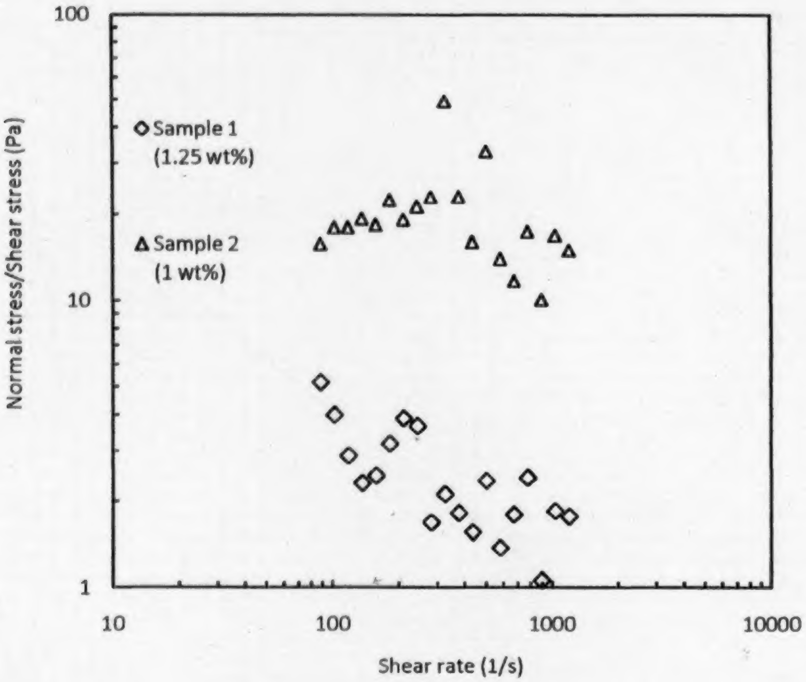

Fig. 5-12 The ratio between Normal force and shear stress for aqueous solutions of sample 1 (1.25 wt %) and sample 2 (1 wt %)

- **Relaxation time**

Relaxation time of the two solutions calculated by Eq. 6-3 is compared in Fig. 5-13. Relaxation time of the two solutions considerably decreases by increasing the shear rate. Aqueous solution of sample 2 (1 wt %) shows higher relaxation time values compared to that of aqueous solution of sample 1 (1.25 wt %).

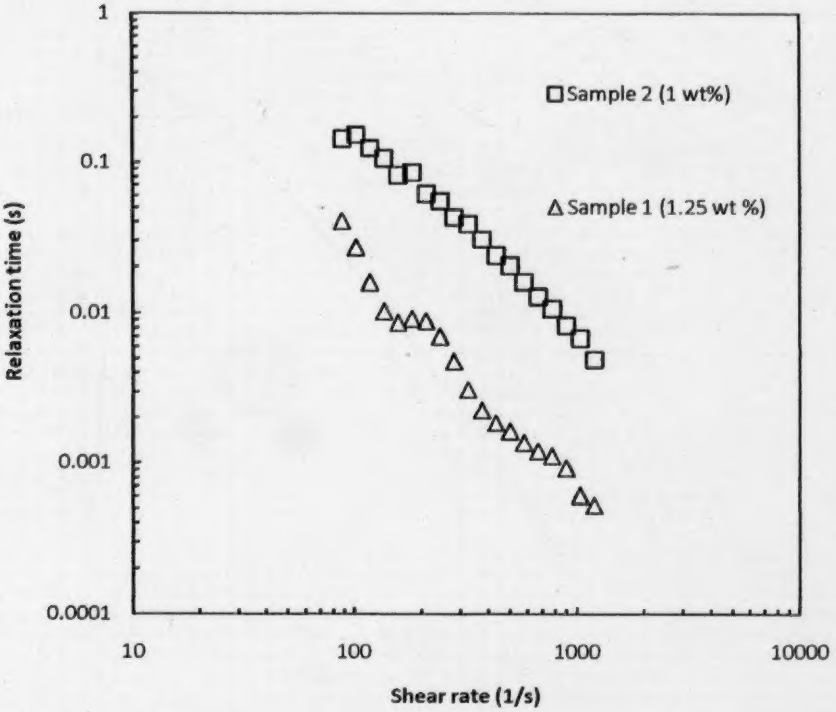

Fig. 5-13 Relaxation time vs. shear rate for aqueous solutions of sample 1 (1.25 wt %) and sample 2 (1 wt %)

5.4.2.2 Pressure drop in radial pack

The two sample solutions are anticipated to present similar pressure drop-flow rate profiles according to Darcy law. Fig. 5-14 compares pressure drop of the two solutions during flow in radial porous media with the permeability of around 0.12 Darcy.

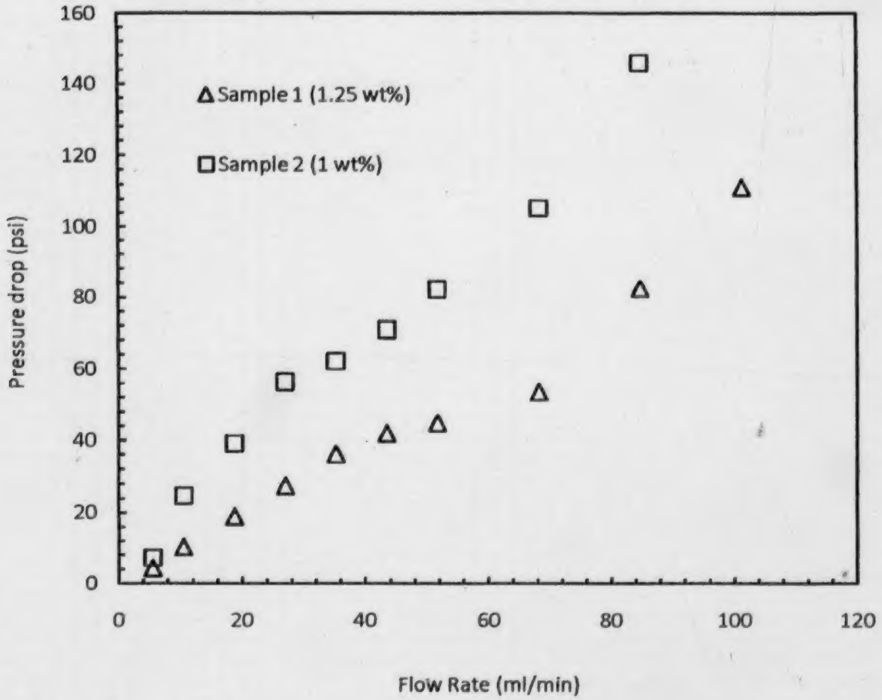

Fig. 5-14 Comparison between pressure drop of sample 1 (1.25 wt %) and sample 2 (1 wt %) during flow in radial porous media (0.12 Darcy)

Three different regions could be considered in pressure drop-flow rate profile of the two solutions.

1. Linear behavior (Low flow rate)
2. Shear thinning behavior (Medium flow rate)
3. Dominant elastic effects (High flow rate)

Although samples 1 and 2 presented similar shear viscosity in viscometry test, their pressure drop-flow rate profiles are different:

1. Pressure values of sample 2 are higher than that of sample 1. The separation between the pressure data of the two solutions increases as flow rate increases.
2. The slope of the linear part of the profile in case of sample 2 is higher than that of sample 1.

3. The shear thinning region of sample 1 is larger than that of sample 2.
4. The region of dominant elastic effects in profile of sample 2 begins at lower flow rates compared to that of sample 1.

5.4.2.3 Comparison of rheological behaviors of sample 1 (1.5 wt %) and sample 2 (1 wt %)

- **Shear viscosity**

For further investigation of the elastic effects on pressure drop in porous media, the flow experiments were also conducted by using 1.5 wt% aqueous solution of sample 1. By increasing the concentration of sample 1, shear stress and shear viscosity were considerably increased as shown in Fig. 5-15 and Fig. 5-16 respectively.

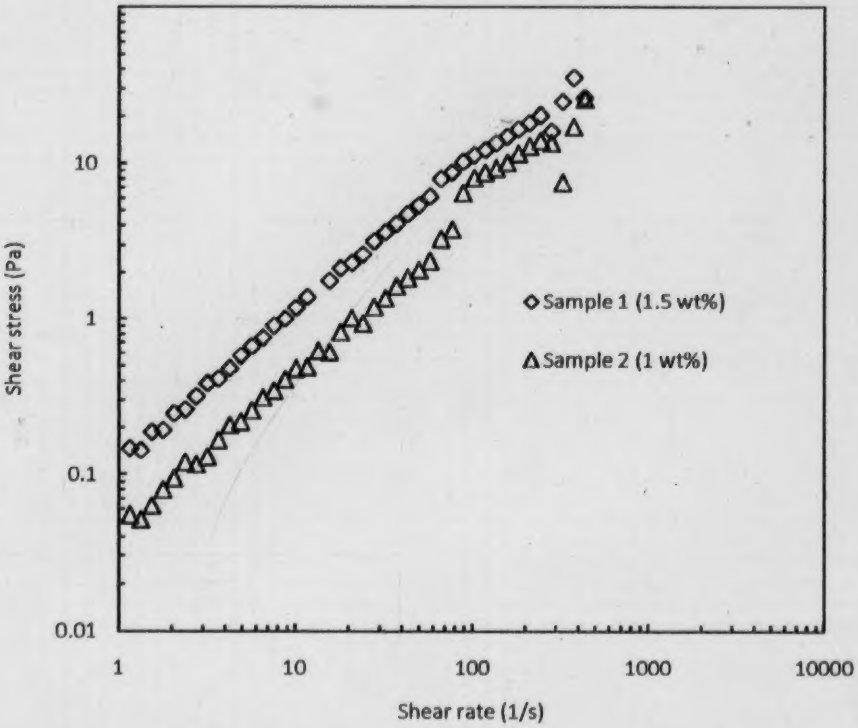

Fig. 5-15 Shear stress versus shear rate for aqueous solutions of sample 1 (1.5 wt %) and sample 2 (1 wt %)

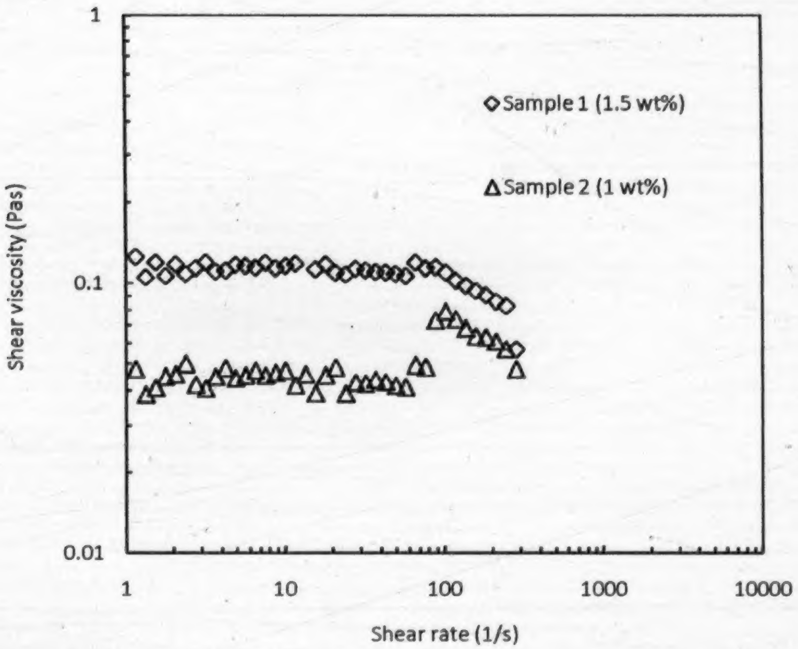

Fig. 5-16 Shear viscosity versus shear rate for aqueous solutions of sample 1 (1.5 wt %) and sample 2 (1 wt %)

- **Normal stress**

Although concentration and shear viscosity of sample 1 is higher than that of sample 2, its normal stress values are significantly lower than that of sample 2 (see Fig. 5-17). It shows the very strong of elastic behavior of sample 2.

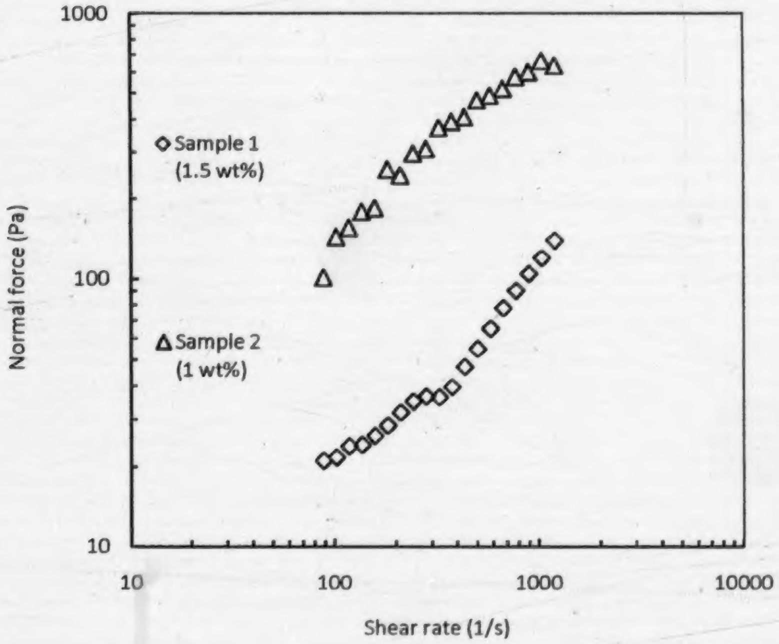

Fig. 5-17 Normal force versus shear rate for aqueous solutions of sample 1 (1.5 wt %) and sample 2 (1 wt %)

Significant differences in elastic properties of sample 2 (1 wt %) compared to that of sample 1 (1.5 wt %) are revealed in Fig. 5-18. Although shear viscosity of sample 2 (1 wt %) is considerably lower than that of sample 1 (1.5 wt %), the value of N_1/τ in case of sample 2 is around one order of magnitude higher than that of sample 1 (1.5 wt%).

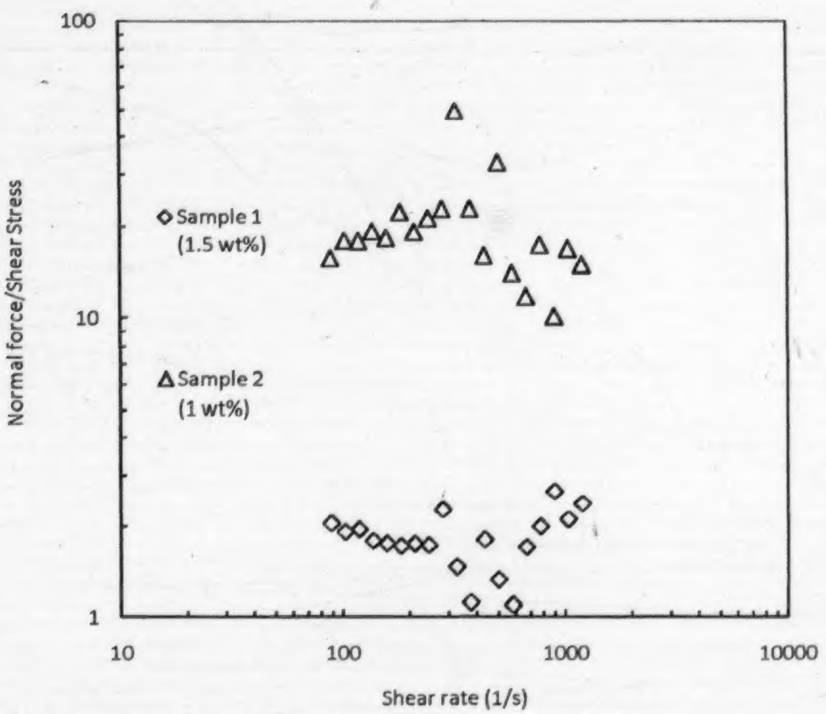

Fig. 5-18 The ratio between Normal force and shear stress for aqueous solutions of sample 1 (1.5 wt %) and sample 2 (1 wt %)

- **Relaxation time**

Both concentration and shear viscosity of aqueous solution of sample 1 (1.5 wt %) is considerably higher than that of aqueous solution of sample 2 (1 wt %). However, relaxation time of sample 2 is almost 10 times higher than that of sample 1 (see Fig. 5-19). These results show that the relaxation time of a polymer can be increased by controlling its elastic properties (through increasing the MWD) without increasing the concentration of the polymer and the viscosity of the solution.

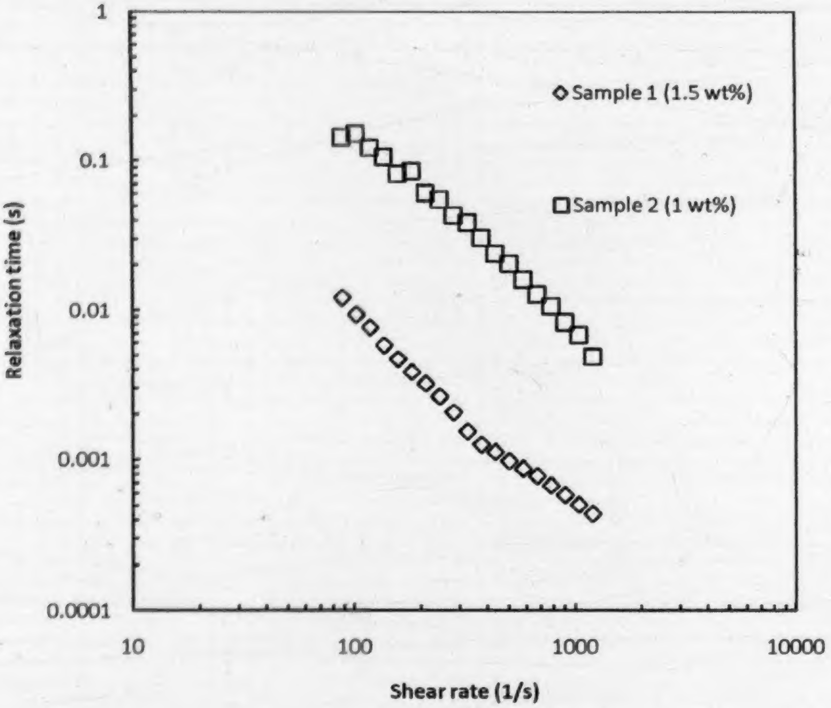

Fig. 5-19 Relaxation time vs. shear rate behavior for aqueous solutions of sample 1 (1.5 wt %) and sample 2 (1 wt %)

5.4.2.4 Pressure drop in radial pack

Fig. 5-20 compares the pressure drop of the two solutions during flow in radial porous media with the permeability of around 0.12 Darcy. Although, Sample 1 (1.5 wt %) is considerably more viscous than sample 2 (1 wt %), its pressure drop in porous media is relatively close to that of sample 2 (1 wt %). Lower shear viscosity of sample 2 is compensated by its dominant elastic effects in comparison to sample 1 (1.5 wt %). Fig. 5-20 shows that the region of dominant elastic effects in pressure profile of sample 2 (1 wt %) occurs at lower flow rates compared to that of sample 1 (1.5 wt %). This indicates dominant elastic effects of sample 2 during flow in porous media in comparison to sample 1.

These results also confirm that pressure drop of a certain polymer based fluid in porous media could be increased by controlling the elastic properties (e.g., increasing the broadness of MWD) without increasing the concentration of the polymer and shear viscosity of the solution.

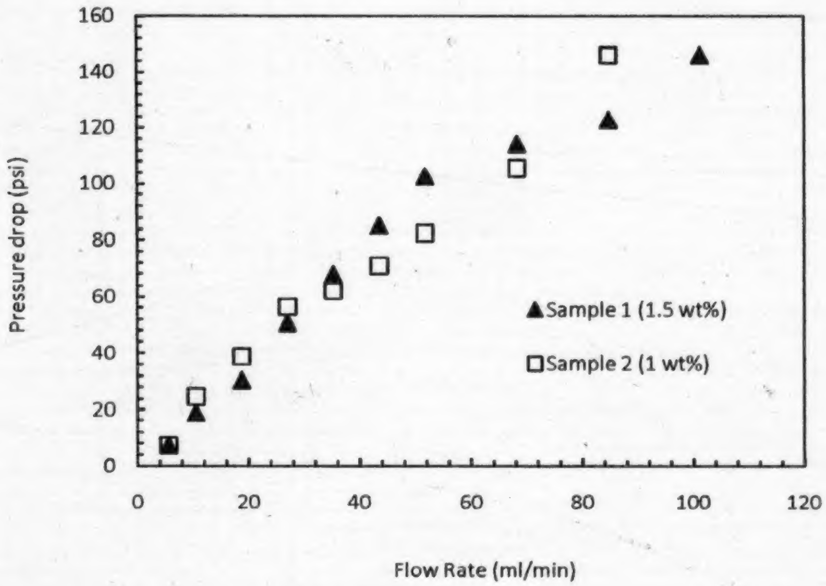

Fig. 5-20 Comparison between pressure drop of sample 1 (1.5 wt %) and sample 2 (1 wt %) during flow in radial porous media (0.12 Darcy)

5.4.3 Permeability impairment

Comparison of the pressure drop due water flow before and after polymer injection would reveal the magnitude of the permeability impairment due to polymer adsorption and/or entrapment. The following procedure was followed to assess the permeability impairment due to flow of polyox solutions.

- Before any polymer injection into the system, pressure drop due to flow of water in original packing was measured.
- After displacement of water by aqueous solution of sample 2 (1 wt %), the pressure drop due to the flow of sample 2 was measured at different flow rates. Following the injection of sample 2, in order to assess the formation damage, the

system was flushed by water. Polymer solution was gradually displaced by water. Water injection was continued until the produced water did not contain any polymer and the pressure drop was stabilized. At this condition the remaining polymer in the system is permanently adsorbed or entrapped in the packed bed. Pressure drop due to flow of water at different flow rates was measured (see Fig. 5-21).

- Sample 1 (1.25 wt %) was injected in the same pack. Stabilized pressure drop due to flow of sample 1 at different flow rates was measured. Finally, the polymer solution (i.e., Sample 1) was displaced by water until no sign of polymer was seen in the produced water. The stabilized pressure drop due to flow of water was measured at different flow rates that is shown in Fig. 5-21.

Fig. 5-21 compares the pressure drop due to flow of water through the pack after injection of each sample solution to the initial pressure drop values in clean core.

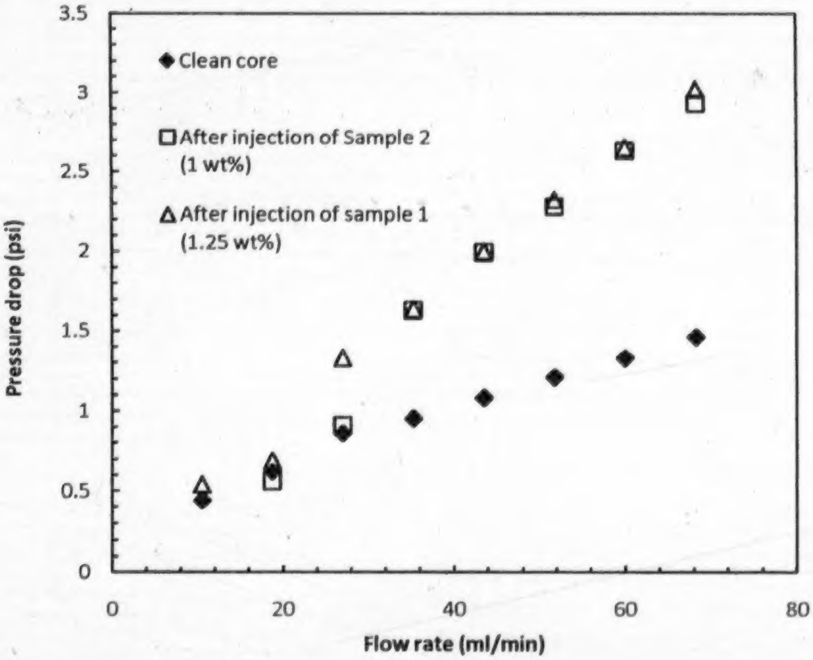

Fig. 5-21 Comparison of pressure drop due to water flow through porous media, in clean core and after injection of samples 1 and 2 (radial cell, 0.12 Darcy)

Comparison of the pressure drop values in Fig. 5-21 indicates that original permeability of the pack is reduced after injection of polymer solution 2. It means that some part of the porous media is blocked due to polymer-wall interaction and entrapment of polyox molecules in narrow channels of porous media. However, it is observed that pressure drop due to water flow after injection of sample 2 (1 wt %) and sample 1 (1.25 wt %) are almost identical. In other words, injecting solution 1 did not cause additional permeability reduction. The following results are obtained from these data:

- Damaging characteristic of both solutions with similar average molecular weight are almost identical.
- Although the permeability of original pack reduces by first polymer run, additional polymer injection doesn't cause further reduction of permeability.
- Permeabilities of the pack after injection of sample 2 (1 wt %) and sample 1 (1.25 wt %) were measured to be identical. Therefore, the difference between pressure

drop values for the flow of two solutions is due to effects other than polymer adsorption and/or entrapment in the pore space.

5.5 Discussion

Based on the results from core flow experiment with samples 1 and 2 the following conclusions can be offered:

- Pressure drop due to the flow of the polyox solutions linearly increase at low flow rates. After the linear region, the rate of pressure increase gradually decreases because of the shear thinning behavior of the solution. Further increase of flow rate beyond a critical value results in thickening behavior (dominant elastic effects) of the fluid in porous media. As the flow rate exceeds a certain limit, the pressure drop due to the flow of polyox solutions in low permeability packing dramatically increases. This upturn of pressure drop curves does not occur in high permeability packing. Therefore, high flow rate and low permeability enhances the elastic effects of polymer flow in porous media.

- The time available for fluid elements to pass through a narrow channel depends on flow rate and average particle size of the packed bed. At higher flow rates and lower permeability systems, fluid elements may not have sufficient time to relax before passing through a new channel. This is more severe when the relaxation time of the fluid is relatively high. At these conditions resistance against flow in porous media may dramatically increase. Such phenomenon was not observed in the results of core flow experiment in high permeability pack (see Fig. 5-8). It means that the average pore size of the porous media is not low enough to restrict the time available for fluid elements to relax.

- Relaxation time of polymeric systems with broad MWD is higher than that of narrow MWD systems measured in uniaxial elongational flow (Plog et al. 2005). Polyox solution with broad MWD showed higher relaxation time values compared to that of narrow MWD solutions (see Fig. 5-13 Fig. 5-19). It may take longer time for elements of sample 2 to relax the stresses induced during flow through a narrow channel of porous media. The upturn observed in pressure drop curve of sample 2 occurs at lower flow rate compared to sample 1. Therefore, in addition to permeability and flow rate, elastic properties of the polymer also influence the occurrence of increased rate of pressure drop. In comparison to sample 1, it takes longer time for elements of sample 2 to relax after each expansion and contraction during flow in narrow channels of porous media. This causes additional resistance against flow of sample 2 through porous media especially at high flow rates and low permeability.

- Drastic pressure drop at flow rates higher than the critical flow rate could be considered as Deborah number effect. This dimensionless number is proportional to the relaxation time and velocity of the fluid (see Eq. 2-21). Deborah number of sample 2 with broader molecular weight distribution is higher than that of sample 1 with narrow MWD (see Table 6-3 and Table 6-4). This is in agreement with earlier occurrence of upturn in pressure curve of sample 2 compared to sample 1. These results show that the Deborah number related to the flow of a polymer solution through porous media could be enhanced at constant average molecular weight (i.e., constant shear viscosity) by increasing the molecular weight distribution.

- Although the drastic pressure drop starts when flow rate exceeds the critical value, the separation between pressure drop-flow rate profiles for solutions of samples 1 and 2 is observed over the entire range of flow rate. It should be noted that the normal stresses of sample 2 solutions are considerably higher than the shear stresses for all shear rates applied in the experiments. Therefore, extensional viscosity of elastic polyox solution (sample 2) could be important for the whole range of flow rates used in these experiments. This explains the difference between pressure drop values of the two sample solutions. This effect could be considered as extensional viscosity or normal force effect.

- Based on the Darcy equation, pressure drop-flow rate profiles of sample solutions with similar average molecular weight (i.e., similar shear viscosity) should be almost the same. The difference between pressure drop of sample solutions with similar shear viscosity in porous media could be due to the following effects:

1. Extensional viscosity effect
2. Deborah number effect

- Pressure drop of aqueous solutions of sample 2 with broader MWD is considerably higher than sample 1 aqueous solutions with narrow MWD. However, considering the similar shear viscosity of the two solutions, Darcy equation predicts similar values of pressure drop for the two solutions. By increasing the MWD of a polymeric system while keeping the average molecular weight (and consequently shear viscosity) constant, pressure drop in porous media could be significantly increased without having additional increase of the shear viscosity. It has been shown in literature that sample polymers with broader MWD exhibit higher extensional viscosity and extensional relaxation time. Therefore, extensional viscosity effect and Deborah number effect (that result in extra pressure drop in porous media) could be enhanced by using polymeric systems with broader MWD.

- In conclusion, the following schematics shown in Fig. 5-22 and Fig. 5-23 are suggested for pressure drop-flow rate profiles observed due to the flow of polyox solutions through porous media.

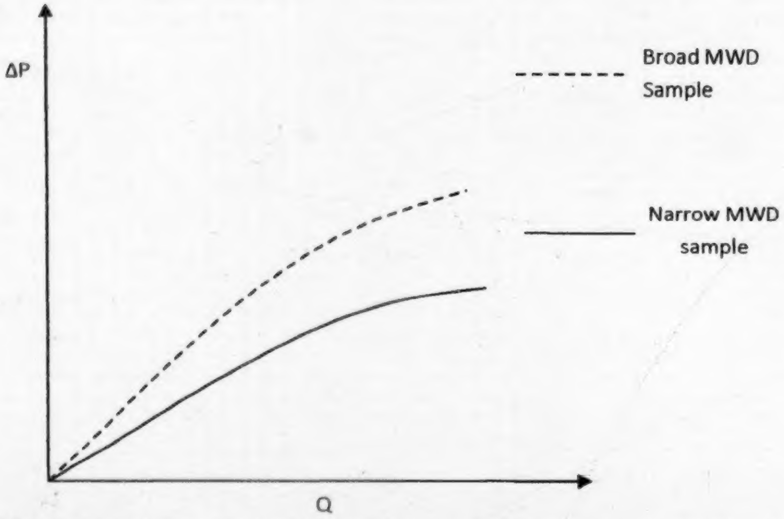

Fig. 5-22 Schematic comparison between pressure drop-flow rate profile of two different polymer solutions with similar average molecular weight and different elastic properties (High permeability porous media)

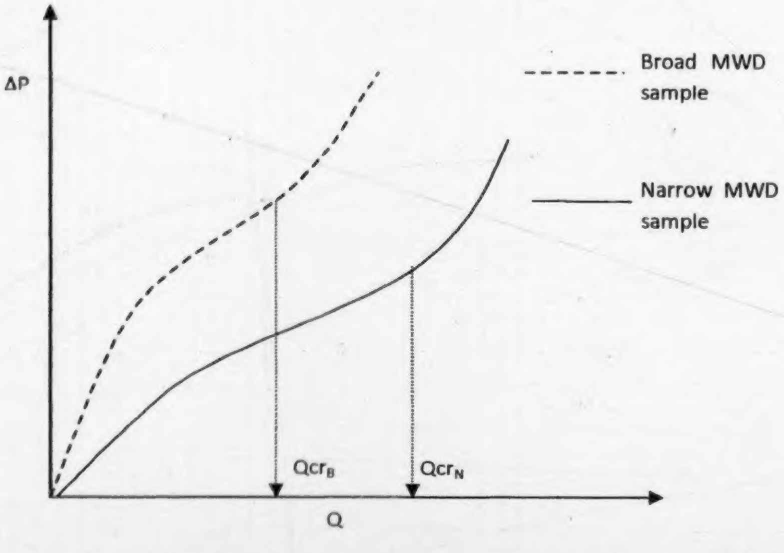

Fig. 5-23 Schematic comparison between pressure drop-flow rate profile of two different polymer solutions with similar average molecular weight and different elastic properties (Low permeability porous media)

CHAPTER 6

COMPARISON OF EXPERIMENTAL DATA AND THEORETICAL MODELS

In this chapter, shear and normal stress values of polyox solutions is modeled by power law relationship.

It is shown theoretically that extensional viscosity of viscoelastic fluids is strongly dependent of Deborah number. Deborah number related to core flow experiments is compared to critical values given in literature.

Measured values of pressure drop due to flow of different polyox solutions in radial pack is compared to predicted values using Darcy equation. Darcy equation is modified to account for elastic effects of polyox solutions.

6.1 Modeling of rheological properties of 3 wt % aqueous polyox solutions

Shear stress vs. shear rate behavior of the two polyox solutions can be described by power law relationship (Fig. 6-1 and Fig. 6-2).

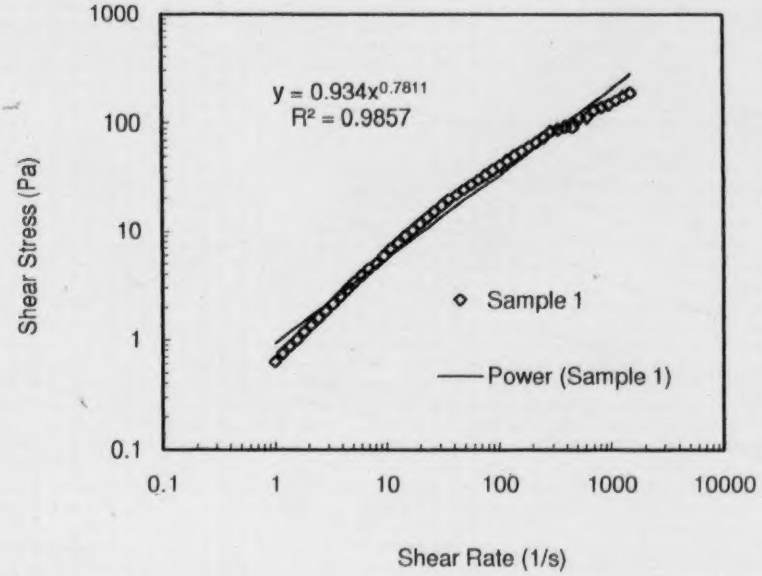

Fig. 6-1 Fitting power law model to experimental values of shear stress vs. shear rate (Sample 1)

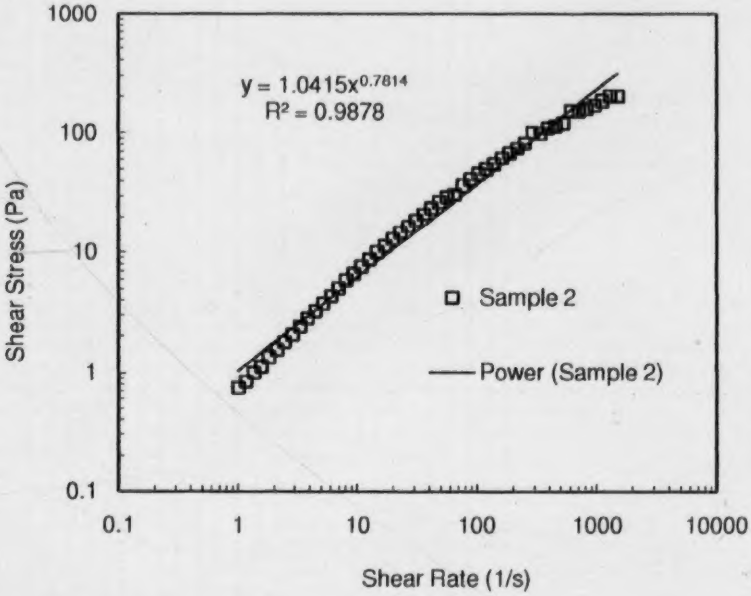

Fig. 6-2 Fitting power law model to experimental values of shear stress vs. shear rate (Sample 2)

Power law model for shear stress is given by the following equation.

$$\tau = m\,\dot{\gamma}^{n} \qquad 6\text{-}1$$

Table 6-1 lists the values of power law constants for the two sample solutions. The power law exponent (n value) of the two solutions is equal. This is in agreement with similar shear thinning behavior of the two solutions shown in Fig. 5-4. However, the power law index (m) of sample 2 is slightly higher. This is also shown by higher value of zero shear viscosity of sample 2 (see Fig. 5-4).

Table 6-1 Power law parameters for shear stress of aqueous solutions of samples 1 and 2 (3 wt. %)

Sample	**m**	**n**
Sample 1	0.934	0.781
Sample 2	1.041	0.781

Fig. 6-3 shows the power law models fit to the experimental values of normal stress of the two solutions.

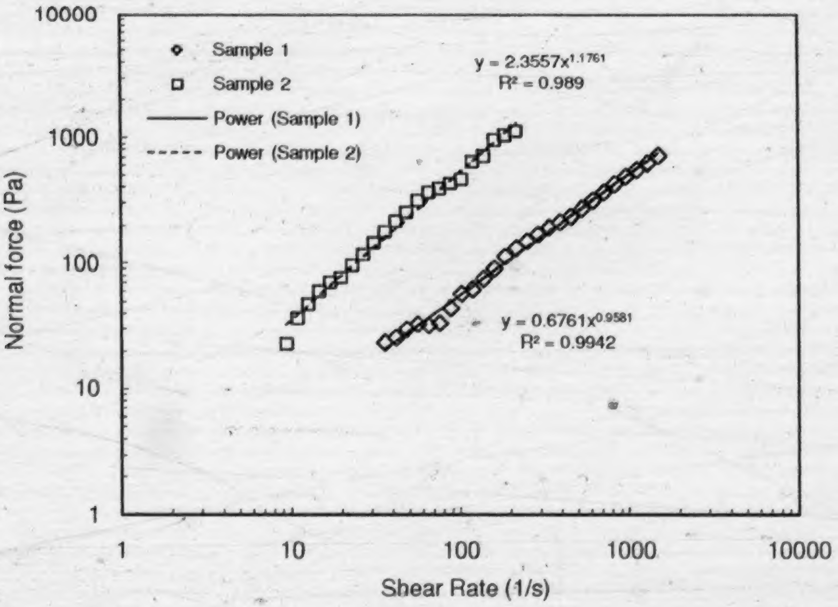

Fig. 6-3 Fitting power law model to experimental values of normal force vs. shear rate

It is suggested that variation of the normal stress as a function of shear rate could also be modeled by a power law relationship.

$$N_1 = m_1 \dot{\gamma}^{n_1} \qquad 6\text{-}2$$

Table 6-2 lists power law constants of Eq. 6-2 for the two sample solutions.

Table 6-2 Power law parameters for first normal stress difference of aqueous solutions of samples 1 and 2 (3 wt. %)

Sample	m_1	n_1
Sample 1	0.676	0.958
Sample 2	2.355	1.176

The value of n_1 is higher than n for both samples 1 and 2. It means that the sensitivity of normal stress to shear rate is more than that of shear stress for both solutions.

Normal stress measured in shear flow could be considered as an indication of elastic properties of polymer solutions. Sample 2 containing large polyox molecules (WSR 308) is expected to behave more elastically that is also revealed from its normal stress behavior. According to Maxwell model first normal stress is related to other rheological properties in simple shear flow by:

$$N_1 = -2\,\theta\mu_0\dot{\gamma}^2 \tag{6-3}$$

Eq. 6-3 shows that the ratio between first normal stress values of sample solutions with similar shear viscosity may be proportional to their relaxation time ratio. According to Eq.6-3 the first normal stress is proportional to shear rate powered by 2. However, the values of n_1 calculated from experimental data are less than 2 for both solutions. This difference could be explained by considering the definition of relaxation time, θ, based on the Maxwell model:

$$\theta = \frac{\mu}{G} \tag{6-4}$$

Elastic modulus of polymeric systems increases with increasing shear rate while, due to shear thinning behavior of polymer solutions, shear viscosity decreases with increasing shear rate. Therefore, relaxation time, θ, is a decreasing function of shear rate and consequently n_1 is anticipated to be less than 2.

6.2 Equivalent Trouton Ratio

By comparing power law models for variation of normal stress and shear stress with shear rate, the equivalent Trouton ratio , $\frac{N_1}{\tau}$, could be related to shear rate also by a power law equation:

$$\frac{N_1}{\tau} = \frac{m_1}{m}\,\dot{\gamma}^{n_1-n} \tag{6-5}$$

Therefore, Eq. 6-5 may also be representative of equivalent Trouton ratio of polymer solutions as a function of shear rate. It should be noted that Eq. 6-5 explains viscoelastic behavior of polymer solutions at shear rates where power law model is valid for both N_1 and τ. The values of $\frac{N_1}{\tau}$ for aqueous solution (3 wt %) of sample 2 with significant elastic effects could be described as a function of shear rate by the following power law relationship:

$$\frac{N_1}{\tau} = 2.262\,\dot{\gamma}^{0.395} \qquad \text{6-6}$$

Fig. 6-4 shows that experimental values of $\frac{N_1}{\tau}$ of sample 2 are reasonably close to the predicted values using Eq. 6-6.

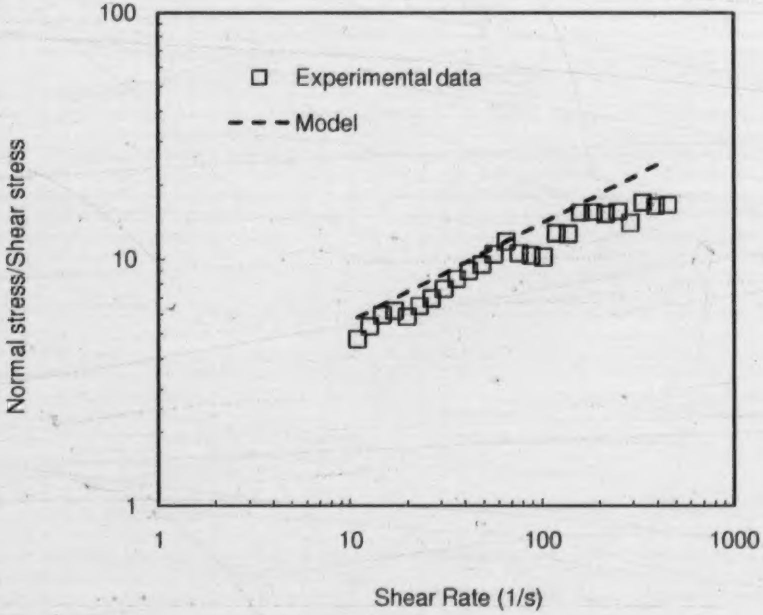

Fig. 6-4 Comparison of measured values of $\frac{N_1}{\tau}$ and predicted values (Eq. 6-6) for aqueous solution of sample 2 (3 wt %)

Extensional viscosity of low concentration polymer solution is very difficult to measure directly. The procedure explained in this section could be used to obtain reasonable estimate of the extensional viscosity in the absence of direct measurement data.

6.2 Critical Flow rate

Deborah number represents the ratio between relaxation time of the fluid and the characteristic time of the experiment. The higher the Deborah number the more elastic would be the behavior of fluid in porous media. Therefore, polymer solution with higher relaxation time behaves more elastically in porous media compared to the one with lower relaxation time. Dramatic pressure drop occurs when Deborah number exceeds the critical value. Such phenomenon could be enhanced by increasing the relaxation time of the solution, increasing the flow rate and/or reducing the permeability.

Savins (1969) and Wissler et al. (1971) correlated the additional pressure drop of a viscoelastic fluid in porous media to Deborah number. Sadowski et al. (1965) experimentally showed that elastic effects are likely to be important at Deborah number of about 0.1. According to Marshal et al. (1966) the critical value of the Deborah number at which appreciable influences of the fluid elasticity are first felt is approximately 0.05-0.06. Their analysis suggested that major elastic effects may be expected to be seen at Deborah number levels in the range of 0.1 to 1.0.

Dramatic pressure drop due to the flow of polyox solutions was observed in case of low permeability pack (0.12 Darcy). This effect was more evident in case of 1 wt % aqueous solution of sample 1. However, this effect was not observed in the results of core flow experiment using high permeability pack (8.9 Darcy).

Denn et al. (1971) suggested the following expression representing tensile stress growth of a viscoelastic fluid in extension.

$$\tau_{11} - \tau_{22} = N_1 = \frac{3\mu\dot{\varepsilon}}{(1-2\theta\dot{\varepsilon})(1+\theta\dot{\varepsilon})} - \frac{2\mu\dot{\varepsilon}}{(1-2\theta\dot{\varepsilon})}\exp\left(-(1-2\theta\dot{\varepsilon})\,{}^{t}/_{\theta}\right) - \frac{\mu\dot{\varepsilon}}{(1+\theta\dot{\varepsilon})}\exp\left(-(1+\theta\dot{\varepsilon})\,{}^{t}/_{\theta}\right) \qquad \text{6-7}$$

Where, $\dot{\varepsilon}$ is the strain rate. This expression highlights that tension growth in a viscoelastic fluid at a certain time strongly depends on $\theta\dot{\varepsilon}$. This term is the product of relaxation time, θ, and strain rate, $\dot{\varepsilon}$, and could be interpreted as the Deborah number of the flow system. Although, in Eq. 6-7 normal stress is a function of time, if $\theta\dot{\varepsilon} < 1/2$ steady state condition is expected after a transient period. Introducing Eq. 6-7 in the definition of extensional viscosity (Eq. 2-10) and Trouton ratio (Eq. 2-12), the following equations are presented for extensional viscosity and Trouton ratio.

$$\mu_e = \mu[\frac{3}{(1-2\theta\dot{\varepsilon})(1+\theta\dot{\varepsilon})} - \frac{2}{(1-2\theta\dot{\varepsilon})}\exp(-(1-2\theta\dot{\varepsilon})\,{}^{t}/_{\theta}) - \frac{1}{(1+\theta\dot{\varepsilon})}\exp(-(1+\theta\dot{\varepsilon})\,{}^{t}/_{\theta})] \tag{6-8}$$

$$Tr = \frac{3}{(1-2\theta\dot{\varepsilon})(1+\theta\dot{\varepsilon})} - \frac{2}{(1-2\theta\dot{\varepsilon})}\exp(-(1-2\theta\dot{\varepsilon})\,{}^{t}/_{\theta}) - \frac{1}{(1+\theta\dot{\varepsilon})}\exp(-(1+\theta\dot{\varepsilon})\,{}^{t}/_{\theta}) \tag{6-9}$$

Fig. 6-5 shows the variation of Trouton ratio with respect to product of strain rate and relaxation time, which can also be considered as the Deborah number.

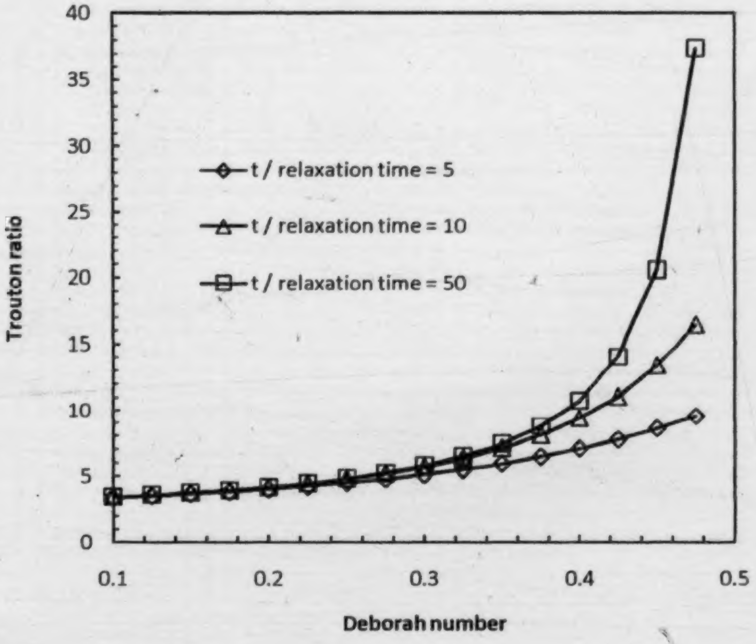

Fig. 6-5 Trouton ratio versus Deborah number (constant strain rate)

The figure 6-5 highlights that Trouton ratio gradually increases with increasing the Deborah number. As Deborah number exceeds the critical value of around 0.5 the Trouton ratio sharply increases. This indicates high values of extensional viscosity in this region. Therefore, a proper estimate of Deborah number corresponding to experimental conditions is required to decide whether extensional viscosity is likely to be important.

Eq. 6-7 is based on constant strain rate, while in porous media deformation rate depends on flow geometry. Gupta et al. (1985) suggested the following expression for "trumped" shape during fluid convergence into a narrow channel.

$$r = r_{max}\exp\left(-\dot{\varepsilon}t/2\right) \qquad 6\text{-}10$$

Therefore, the total time for fluid to pass through the converging part of channel is given by:

$$\delta = \frac{2}{\dot{\varepsilon}}\ln\left(\frac{r_{max}}{r_{min}}\right) = \frac{a}{\dot{\varepsilon}} \qquad 6\text{-}11$$

In Eq. 6-11 r_{max} and r_{min} are maximum channel radius and the radius at the throat of converging-diverging channel respectively. Combining Eq. 6-7 and Eq.6-11, Eq. 6-12 is presented for the maximum Trouton ratio that may occur at the throat of the channel.

$$Tr = \frac{3}{(1 - 2\,a\,\theta/\delta)\,(1 + a\,\theta/\delta)} - \frac{2}{(1 - 2\,a\,\theta/\delta)}\exp(2\,a - {}^{\delta}/_{\theta}) - \frac{1}{(1 + a\,\theta/\delta)}\exp(-\mathrm{a} - {}^{\delta}/_{\theta}) \qquad 6\text{-}12$$

Fig. 6-6 shows the behavior of Trouton ratio as a function of Deborah number and dimensionless number "a" according to Eq.6-12.

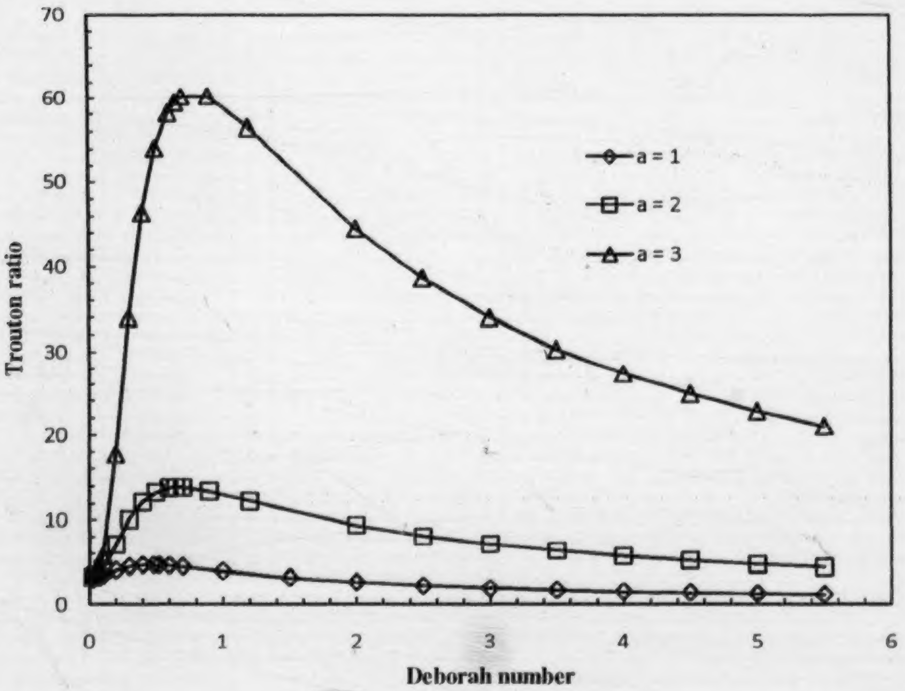

Fig. 6-6 Trouton ratio versus Deborah number at different flow geometries

It is seen in Fig. 6-6 that the ratio between the maximum and minimum pore throat diameter strongly influences the value of Trouton ratio. According to Gupta et al. (1985) when "a" is lower than unity ($r_{max}/r_{min} \leq 1.65$) regardless of flow rate and fluid properties the time required for stress build up is not enough and any tension thickening would not occur in porous media. Fig. 6-6 highlights that Trouton ratio increases considerably with increasing "a" value. This is an anticipated behavior, because the extensional deformation increases with increasing the ratio between maximum and minimum radius of tortuous channels of porous media. Therefore, extensional viscosity is strongly dependent on the tortuous nature of porous media. At higher values of "a" there would be more time available for stresses to build up. While, at low values of constant "a" the time for stress build up is limited. Therefore, higher stretching rate would be needed to reach the same values of Trouton at higher "a" values. Deiber et al. (1981) studied the fluid flow through a tube with sinusoidal variable diameter and concluded that at constant Deborah number the product of Reynolds number and friction factor increases with diameter amplitude and is independent of wavelength. However, actual flow conditions in porous media are not purely extensional (and may not obey simplified kinetics suggested by pore geometry).

It is also concluded from Fig. 6-6 that, extensional viscosity significantly increases with increasing Deborah number at low Deborah numbers. Therefore, increasing Deborah number until certain values results in higher resistance forces against viscoelastic flow in porous media. Wissler et al. (1971) suggested the following expression for flow of a viscoelastic fluid in packed beds.

$$f \cdot Re = 1 + A \cdot De^2 \qquad \text{6-13}$$

According to this equation the product of friction factor and Reynolds number depends on Deborah number and a constant "A" which can vary between 10 and 90. The variability of "A" is due to the dependency of elastic stresses on pore geometry. Deborah number may increase through:

1) Increasing relaxation time
2) Decreasing the phenomenon characteristic time or increasing strain rate.

However, Fig. 6-6 shows that additional increase of Deborah number beyond a critical value considerably reduces the Trouton ratio. A maximum value of Trouton ratio is observed in each curve that is more pronounced at higher values of "a". Therefore, in each flow geometry there may be a specific flow rate (i.e., Deborah number) that results in significant dominance of extensional viscosity. Although increasing flow rate and consequently Deborah number leads to dominance of elastic behavior of polymer solutions, required time for stresses to build up may also reduce as Deborah number increases. However, considering low flow rates in porous media, increasing the Deborah number will result in higher pressure loss.

In order to investigate the effect Deborah number on drastic pressure drop in porous media, relaxation time, θ, of polyox solutions was measured at equivalent shear rate corresponding to the beginning of dominant elastic effects region (see Table 6-3).

Table 6-3 Rheological properties and relaxation times of polyox solutions at equivalent shear rate where dramatic pressure drop is observed.

Fluid	**K (Darcy)**	**D_p (mic) Eq. (2-22)**	**Q_{cr} (ml/min)**	**$\dot{\gamma}_{cr}$ (1/s)**	**$N_1(\dot{\gamma}_{cr})$ (Pa)**	**μ_0 (Pa.s)**	**$\theta(\dot{\gamma}_{cr}) = N_1/(2\mu_0\dot{\gamma}^2)$ (s)**
Sample 1 (1.25 wt %)	0.12	6.6	65	253.5	35	0.045	0.006
Sample 1 (1.5 wt %)	0.12	6.6	85	331.5	36.5	0.11	0.0015
Sample 2 (1 wt %)	**0.12**	**6.6**	**35**	**136.5**	**178.3**	**0.045**	**0.105**
Sample 1 (3 wt %)	8.9	66.5	> 140	> 67.2	> 32	0.65	< 0.0055
Sample 2 (3 wt %)	8.9	66.5	> 140	> 67.2	> 369.3	0.72	< 0.057

Table 6-4 lists the calculated values of Deborah number for polyox solutions measured at the entrance (Ri), average radius (Rm) and exit (Ro) of the radial pack. Significant increase of pressure drop due to the flow of sample 2 (1 wt %) after the flow rate of about 35 ml/min is in agreement with the calculated values of Deborah number for this solution that is beyond the critical value. The upturn was also clearly observed in pressure drop-flow rate profile of sample 1 (1.25 wt %) that is in agreement with calculated Deborah number values for this solution. The upturn in pressure drop curve of 1.5 wt % aqueous solution (sample 1) was hardly observed at flow rate of around 85 ml/min. Calculated values of Deborah number for this solution is relatively lower than the critical values reported in the literature.

Table 6-4 Calculated values of Deborah number for polyox solutions at different parts of the radial pack

Fluid	**De ($\dot{\gamma}_{cr}$) Eq. (2-21)**		
	R=R_i	**R=R_m**	**R=R_o**
Sample 1 (1.25 wt %)	0.25	0.05	0.03
Sample 1 (1.5 wt %)	0.08	0.02	0.01
Sample 2 (1 wt %)	**2.39**	**0.45**	**0.24**
Sample 1 (3 wt %)	< 0.05	< 0.01	< 0.01
Sample 2 (3 wt %)	< 0.55	< 0.1	< 0.06

6.3 Comparison of experimental pressure drop values with theoretical values calculated from Darcy equation in radial systems

In the following sections, pressure drop due to flow of polyox solutions in radial pack is compared to theoretical values.

6.3.1 High permeability-high polymer concentration case

Darcy equation in radial systems was used to predict pressure drop of the two sample solutions in porous media.

$$\Delta P\ (psi) = \frac{\mu\, Ln\left(\frac{r_e}{r_w}\right)}{2\,\pi\, L\, k}\, Q = \frac{Ln(\frac{4.75}{0.5})}{2 \times \pi \times 8in \times 8.9d}\, \mu \times Q = 0.48\ \times\ \mu(Pas) \times Q({}^{ml}/_{min}) \tag{6-14}$$

Power law model was used to calculate the shear viscosity of the fluid at equivalent shear rates corresponding to each flow rate. In order to compare the pressure values to rheological properties of the sample solutions, pressure values are plotted as a function of equivalent shear rate corresponding to each flow rate. Fig. 6-7 and Fig. 6-8 compares the measured values of pressure drop of samples 1 and 2 to the values predicted by the Darcy equation respectively.

Measured values of pressure drop for sample 1 are almost close to the values predicted by Darcy equation in radial systems. Sample 1 and sample 2 have very similar shear viscosity values. Therefore, they are expected to present similar pressure drop according to Darcy equation. However, pressure drop of sample 2 is considerably higher than the values predicted by Darcy law. This could be explained by the fact that sample 2 shows more elastic behavior than that of sample 1.

Considering the higher values of normal stress of sample 2, its extensional viscosity is anticipated to be higher than that of sample 1. Higher pressure drop of sample 2 in porous media can therefore, be attributed to higher values of its extensional viscosity compared to that of sample 1.

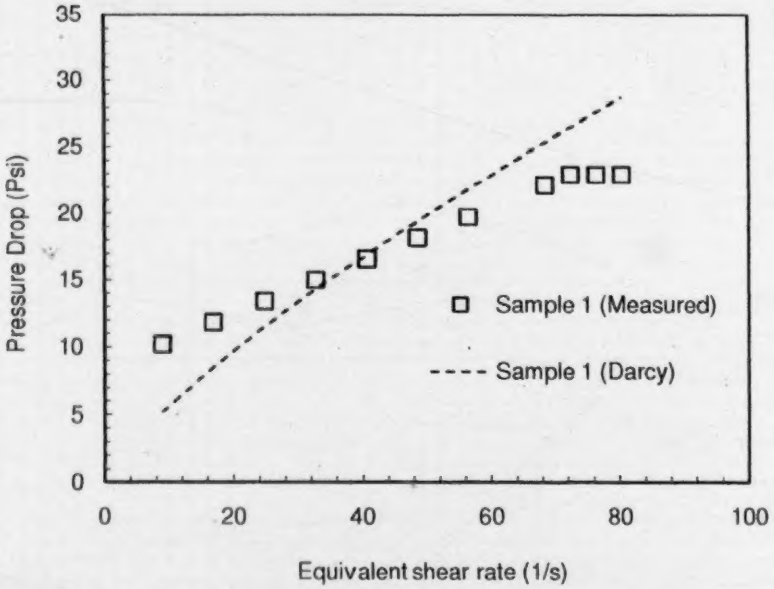

Fig. 6-7 Pressure drop-shear rate for aqueous solutions of sample 1 (3 wt %) - Comparison of experimental results with predicted values from Darcy equation

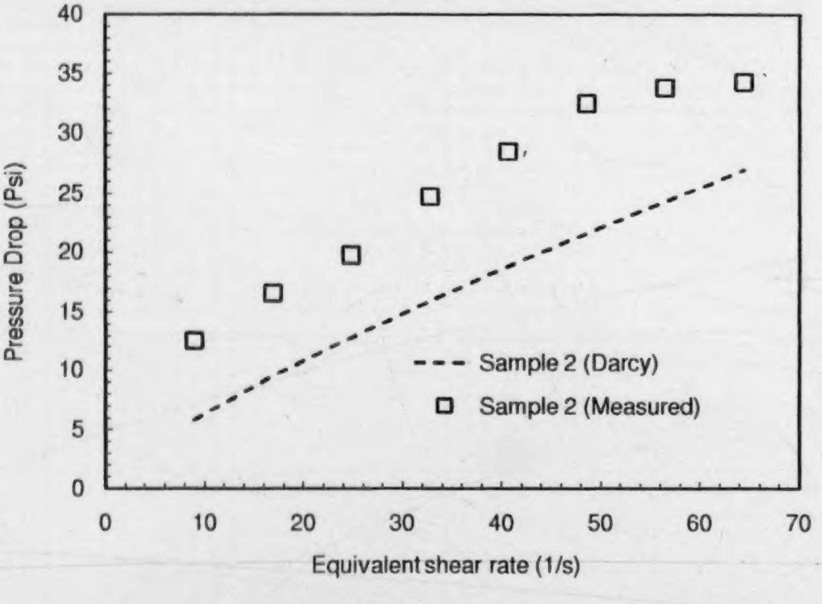

Fig. 6-8 Pressure drop-shear rate for aqueous solutions of sample 2 (3 wt %) and comparison of experimental results with the values predicted from Darcy equation

6.3.2 Low permeability-low polymer concentration case

According to Darcy equation in radial systems, pressure drop in radial packing is related to flow rate and shear viscosity by:

$$\Delta P\ (psi) = \frac{\mu\ Ln\left(\frac{r_e}{r_w}\right)}{2\ \pi\ L\ k}\ Q = \frac{Ln\left(\frac{4.75}{0.5}\right)}{2\times\pi\times 8in\times 0.12\ d}\ \mu\times Q = 28.8\ \times\ \mu(Pas)\times Q(^{ml}/_{min}) \tag{6-15}$$

However, the flow may not be purely radial in the radial packing. In order investigate the validation of Darcy equation, the measured pressure drop values of water in the radial cell were compared with the ones predicted from Darcy equation (Fig. 6-9).

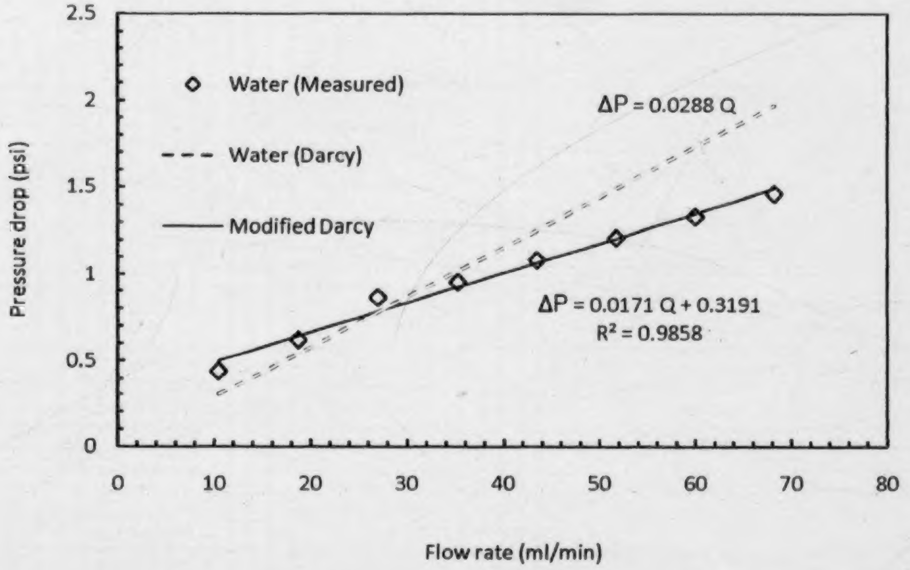

Fig. 6-9 Comparison of measured pressure drop for water flow in radial cell and the ones predicted from Darcy equation (Permeability: 0.12 Darcy)

The slope of pressure drop-flow rate profile of water in radial cell is 0.017. The calculated value of the slope of pressure drop-flow rate linear profile, using Darcy equation in radial systems is 0.029. Therefore, Eq. 6-15 does not correctly predict the flow performance of water in radial cell. The linear profile fit to the experimental data of water pressure drop and flow rate, is considered as the base line for Darcy equation in radial cell. Therefore, Darcy equation in radial cell is modified as follows:

$$\Delta P\ (psi) = \frac{\mu\ Ln\left(\frac{r_e}{r_w}\right)}{2\,\pi\, L\, k}\ Q = 17\ \times\ \mu(Pas) \times Q({}^{ml}/{}_{min}) \qquad 6\text{-}16$$

The pressure drop values (for water flow in radial cell) calculated by using Eq. 6-17 are also shown in Fig. 6-10 (solid line in Fig. 6-10).

The pressure drop values of the polyox solutions during radial flow in low permeability pack (0.12 Darcy) were compared with the values predicted from Darcy equation.

Fig. 6-10 shows that measured values of pressure drop of sample 1 (1.25 wt %) are close to Darcy values upto a certain flow rate. Pressure drop data deviates from Darcy line when the flow rate exceeds a critical value.

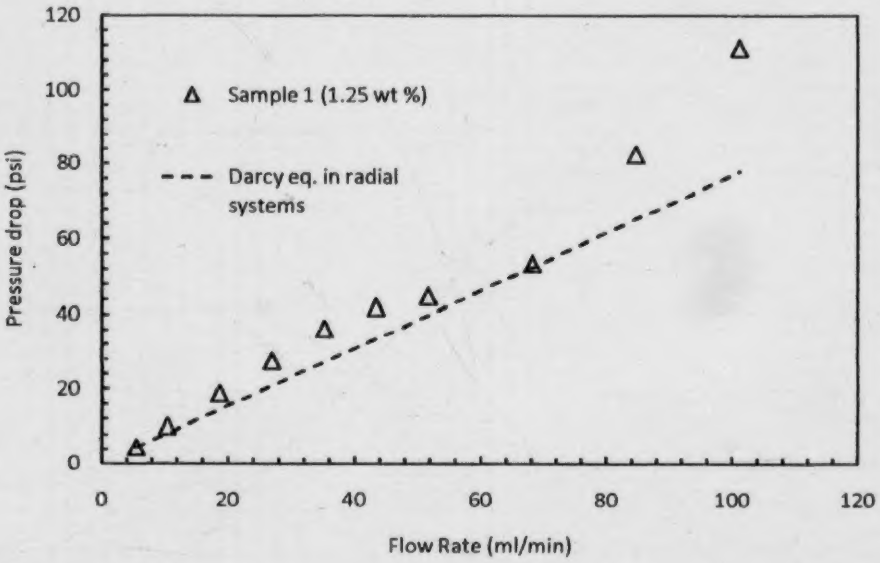

Fig. 6-10 Pressure drop versus flow rate of sample 1 (1.25 wt %) in radial porous media (0.12 Darcy) and comparison with predicted values fromDarcy equation.

Although Normal stress values and consequently extensional viscosity of sample 1 (1.25 wt %) is relatively low, pressure drop values deviate from predicted values obtained from

Darcy equation at high flow rates (region of dominant elastic effects). Considering low values of N_1/τ for this solution (see Fig. 5-12), the effect of extensional viscosity on the pressure drop is expected to be negligible. The upturn observed in pressure drop-flow rate profile can be due to Deborah number effect. Tables Table 6-3 andTable 6-4 show that calculated Deborah number related to flow rate of 65 ml/min is 0.25 at $R=R_i$ and 0.05 at $R=R_m$. Therefore, at flow rates higher than 65 ml/min, Deborah number due to flow of this solution is fairly in the critical range (0.1-1 for major elastic effects) suggested by Marshal et al. (1966).

As shown in Fig. 6-11 Darcy equation provides reasonable estimation of the pressure drop of sample 1 (1.5 wt %) in porous media. The average value of N_1/τ for this solution is about 2 (See Fig. 5-18) that indicates insignificant elastic properties of this solution. The theoretical value of Trouton number for a Newtonian fluid is 3. Therefore, it is anticipated that extensional viscosity does not have significant effect on pressure drop of aqueous solution (1.5 wt %) of sample 1.

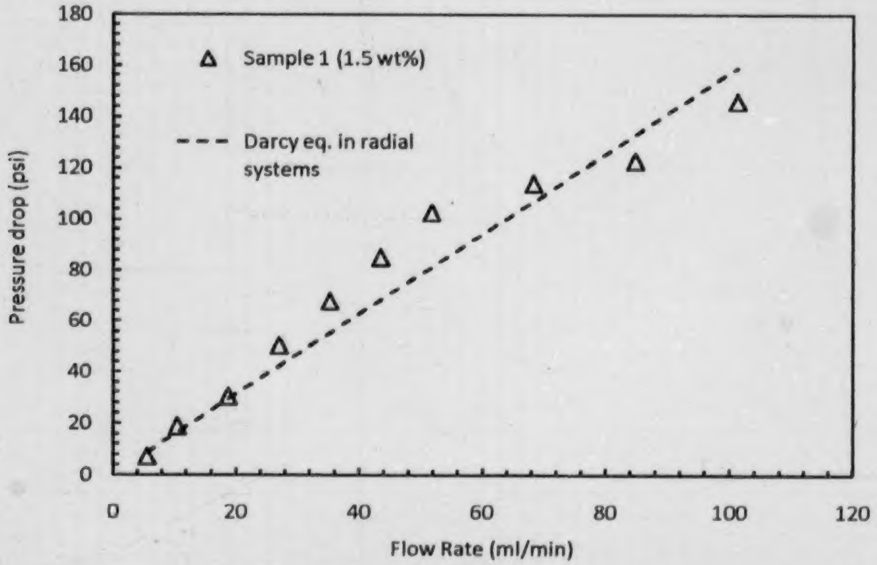

Fig. 6-11 Comparison of measured pressure drop versus flow rate of sample 1 (1.5 wt %) in radial low permeability pack (0.12 Darcy) and predicted values using Darcy equation

The region of significant elastic effects (Deborah number effect) is less dominant in case of 1.5 wt % solution of sample 1 compared to that of 1.25 wt % solution of sample 1. The upturn in the profile of 1.5 wt % solution is weekly observed at the flow rate of 85 ml/min. While the pressure drops of 1.25 wt % solution dramatically increased at flow rates higher than 65 ml/min. In order to explain this, the relaxation time vs. shear rate behavior of these two solutions is compared in Fig. 6-12. Relaxation time of 1.25 wt % solution is relatively lower than that of 1.5 wt% solution. This means that Deborah number related to flow of 1.25 wt % solution in porous media is higher than that of 1.5 wt % solution. Tables Table 6-3 and Table 6-4 show that there is a considerable difference between the calculated Deborah numbers of the two solutions.

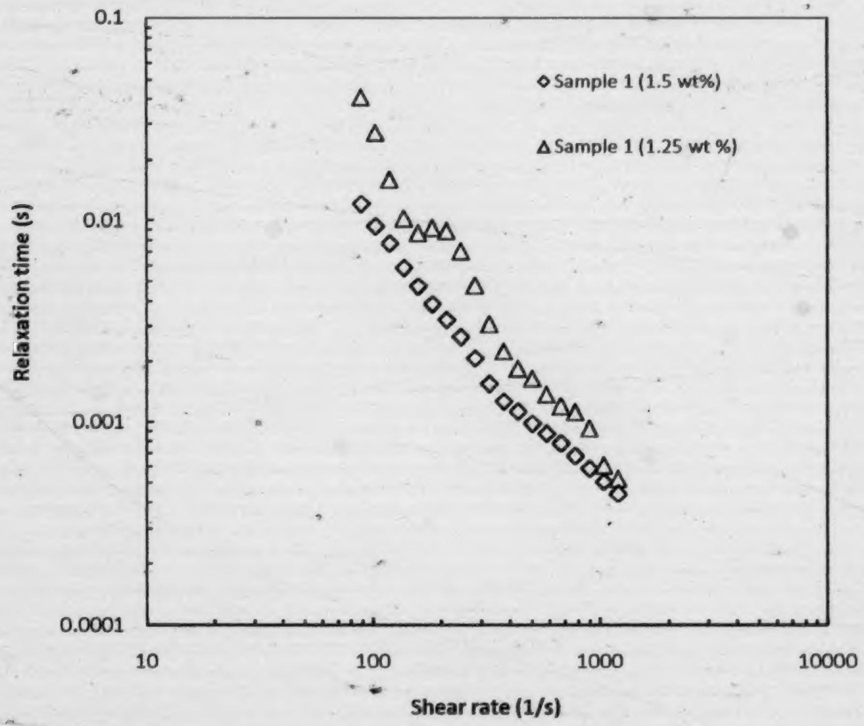

Fig. 6-12 Comparison between relaxation time vs. shear rate behavior of aqueous solutions of sample 1

Insignificant deviation of sample 1 solutions (1.25 wt% and 1.5 wt %) from Darcy equation is in agreement with low values of N_1/τ for these two solutions (see Fig. 5-12 and Fig. 5-18).

Fig. 6-13 shows that there is a significant difference between measured pressure drop of sample 2 (1 wt %) and predicted values from Darcy equation. The following factors can be considered to explain this abnormal behavior:

- The measured values of N_1/τ for this solution are relatively high (see Fig. 5-12). This dimensionless number could be interpreted as Trouton value. Therefore, extensional viscosity is anticipated to influence flow behavior of this solution that is not considered in Darcy equation.
- The relaxation time of this fluid is relatively high (See Fig. 5-13). Therefore, Deborah number related to flow of this solution in porous media is relatively high. Tables Table 6-3 and Table 6-4 show that Deborah number related to flow of this fluid at flow rate of 35 ml/min is considerably high.

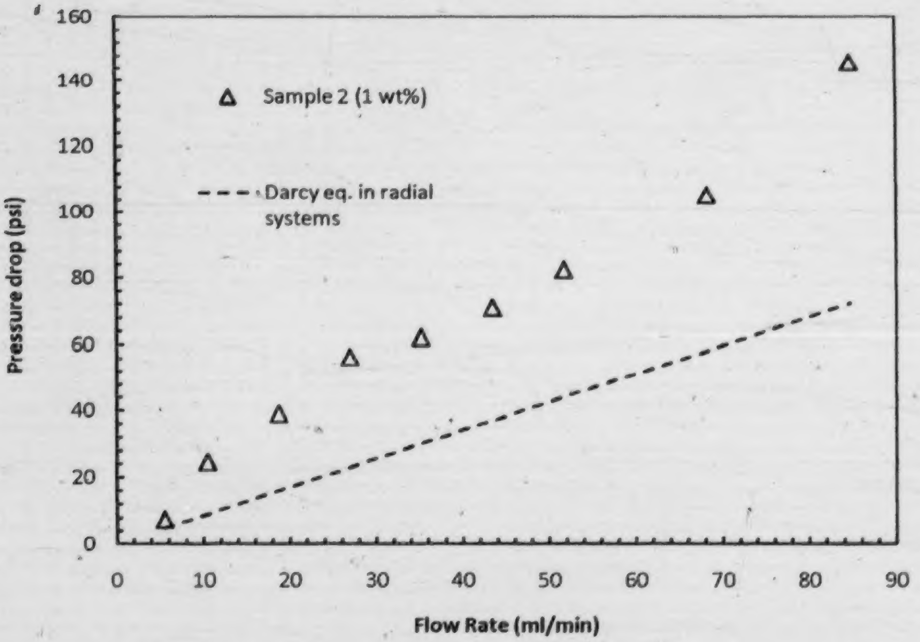

Fig. 6-13 Pressure drop versus flow rate of sample 2 (1 wt %) in radial porous media (0.12 Darcy) and comparison with predicted values from Darcy equation

6.4 Modification of Darcy equation for elastic effects of polyox solutions

The results of the two parts of the core flow experiment (High permeability and Low permeability) revealed the effect of elastic properties of polyox solutions on pressure drop in porous media. The equivalent Trouton ratio, $\frac{N_1}{\tau}$, values of each sample solution were measured at different shear rates (i.e., flow rate). It was observed that pressure profile of sample solutions with low values of N_1/τ (i.e., $N_1/\tau < 5$) approximately follows the Darcy law (see Fig. 6-7Fig. 6-10Fig. 6-11). Aqueous solutions of sample 2 (3 wt% and 1 wt %) with high values of N_1/τ (i.e., $N_1/\tau > 5$) showed significant deviation from Darcy equation (see Fig. 6-8 and Fig. 6-13).

Therefore, pressure drop of polyox solutions with significant elastic effects may be correlated to N_1/τ. The results of core flow experiment for aqueous solutions of sample 2 are summarized in Table 6-5 and Table 6-6.

Table 6-5 Measured pressure drop and predicted values from Darcy equation for sample 2 (3 wt %) in radial packing (8.9 Darcy)

Flow rate (ml/min)	Equivalent shear rate (1/s)	Measured pressure drop (psi)	Darcy pressure drop (psi)	$\Delta P_{measured}/\Delta P_{Darcy}$
18.76	9.0	12.5	5.8	2.16
35.26	16.9	16.57	9.5	1.75
51.76	24.8	19.75	12.8	1.54
68.26	32.8	24.69	15.9	1.55
84.76	40.7	28.46	18.8	1.51
101.26	48.6	32.46	21.6	1.50
117.76	56.5	33.77	24.3	1.39
134.26	64.4	34.24	26.9	1.27

Table 6-6 Measured pressure drop and predicted values from Darcy equation for sample 2 (1 wt %) in radial packing (0.12 Darcy)

Flow rate (ml/min)	Equivalent shear rate (1/s)	Measured pressure drop (psi)	Darcy pressure drop (psi)	$\Delta P_{measured}/\Delta P_{Darcy}$
5.56	21.68	7.2	4.74	1.52
10.51	41	24.53	8.95	2.74
18.76	73.16	38.98	15.98	2.44
27.01	105.34	56.31	23.00	2.45
35.26	137.51	62.09	30.04	2.07
43.51	169.69	70.76	37.07	1.91
51.76	201.86	82.31	44.09	1.87
68.26	266.21	105.42	58.15	1.81
84.76	330.56	145.87	72.21	2.02

Table 6-7 compares the average values of the ratio between measured and calculated pressure drop and N_1/τ for the two solutions. The average value of N_1/τ for 1 wt% solution is about 2 times higher than that of 3 wt% solution. It should be noted that equivalent shear rate of 1 wt % solution (in Low permeability pack) was higher than that of 3 wt % solution (in high permeability pack).

Table 6-7 Comparison between average values of $\Delta P_{measured} / \Delta P_{Darcy}$ and N_1/τ for aqueous solutions of sample 2

Polyox solution	$(\Delta P_{measured} / \Delta P_{Darcy})_{Ave}$	$(N_1/\tau)_{Ave}$
Sample 2 (3 wt %)	1.58	7.9
Sample 2 (1 wt %)	2.1	16.5

Massarani et al (2001) proposed the following expression to predict the pressure drop of a general incompressible fluid flowing through a porous media.

$$\left(\frac{\Delta P}{L}\right) = \frac{\mu(\dot{\gamma}^*)}{k}\left(1 + \frac{c\sqrt{k}\rho V}{\mu(\dot{\gamma}^*)} + \frac{C_{N_1}N_1(\dot{\gamma}^*)}{\tau(\dot{\gamma}^*)} + \frac{C_{N_2}N_2(\dot{\gamma}^*)}{\tau(\dot{\gamma}^*)}\right)V \tag{6-17}$$

$\dot{\gamma}^*$ is characteristic deformation rate in porous media. In this expression viscous forces and inertial effects as well as normal stress differences have been considered in pressure loss calculation. Calculating second normal stress difference is relatively difficult, however, its value is about one order of magnitude less than first Normal stress difference and could be neglected. The velocity of viscoelastic fluids in porous media is relatively low. Therefore, Reynolds number is considerably low in such flow conditions. The calculated values of Reynolds term are lower than normal stress term by several orders of magnitude. Therefore, inertial effects could also be neglected in this expression.

Eq. 6-17 could be simplified as follows:

$$\left(\frac{\Delta P}{L}\right) = \frac{\mu(\dot{\gamma}^*)}{k}\left(1 + \frac{C_{N_1}N_1(\dot{\gamma}^*)}{\tau(\dot{\gamma}^*)}\right)V \tag{6-18}$$

Combining the equation 6-18 with Darcy equation, Eq. 6-19 is obtained to account for additional pressure drop due to viscoelastic effects in porous media.

$$\Delta P_{viscoelastic} = \Delta P_{Darcy}\left(1 + C_N \frac{N_1}{\tau}\right) \tag{6-19}$$

The constant parameter of C_N was calculated using the average values of pressure drop ratio and $\frac{N_1}{\tau}$ measured for the two flow experiments (see Table 6-7). Interestingly, C_N was calculated to be identical (around 0.08) for the two sets of experiments.

Fig. 6-14 and Fig. 6-15 compare the measured values of pressure drop to the predicted values using the suggested model (Eq. 6-19) for 3 wt % and 1 wt % solutions respectively.

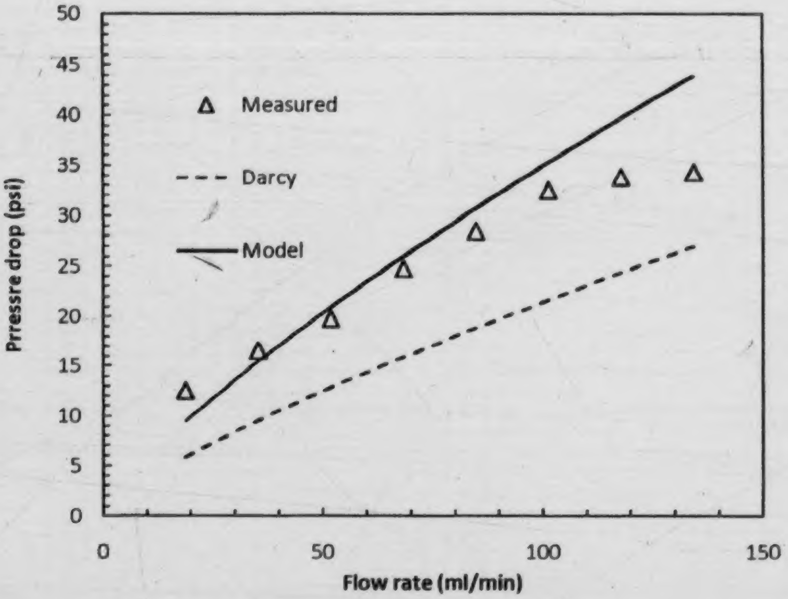

Fig. 6-14 Comparison between measured pressure drop and predicted values using Darcy equation and suggested model (Eq.6-20) for aqueous solutions of sample 2 (3 wt %)

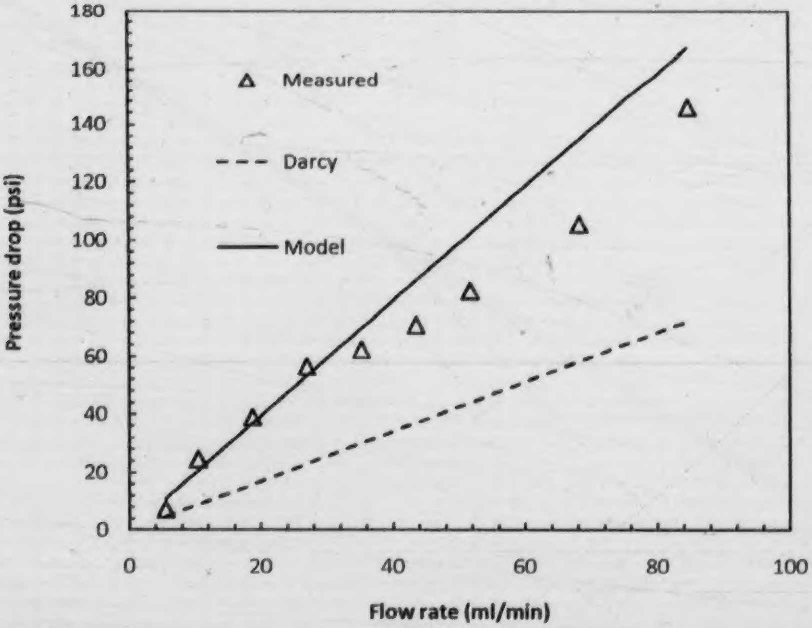

Fig. 6-15 Comparison between measured pressure drop and predicted values using Darcy equation and suggested model (Eq.6-20) for aqueous solutions of sample 2 (1 wt %)

The pressure drop values predicted by Eq. 6-19 are reasonably more accurate than that of Darcy equation. However, in both Fig. 6-14 and Fig. 6-15 experimental data deviate from the suggested viscoelastic model after a certain flow rate. This could be explained by shear thinning of polyox solutions at high shear rates that is not truly accounted for in the proposed viscoelastic model. Darcy values of pressure drop are calculated using the shear viscosity of fluid at equivalent shear rates corresponding to each flow rate. But comparison between experimental data and predicted values using Darcy (for weekly elastic samples) and viscoelastic model (for strongly elastic samples) shows that shear thinning behavior observed in porous media may be stronger than shear thinning behavior measured in viscometry test.

CHAPTER 7

CONCLUSIONS AND RECOMMNEDATIONS

7.1 Conclusions

- The new mixing rule presented for mixture viscosity and molecular weight predicted more accurate values of equivalent viscosity and molecular weight of the mixture compared to existing correlations in the literature that are based on weight average molecular weight.

- It was observed that Polyox blend with broader molecular weight distribution (i.e., higher fraction of macro molecules) has lower values of viscous and elastic modulus as well as higher values of dominant relaxation time and lower relaxation spectra.

- Rheological characteristics of two polymer solutions with similar average molecular weight and different molecular weight distribution (MWD) were compared. Although the two samples showed similar shear viscosity, normal stress and relaxation time values of the sample with broad MWD was significantly higher than that of narrow MWD sample.

- Equivalent Trouton value of broad MWD sample was higher than that of narrow MWD sample. This indicates that extensional viscosity of polyox solutions can be increased by increasing the broadness of MWD at constant shear viscosity.

- Pressure drop-flow rate profile of polyox solutions (3 wt %) in high permeability pack (8.9 Darcy) showed two different regions. Initially, the profile is linear suggesting shear viscosity of the sample does not change significantly. As the flow rate exceed a critical value, however, the shear thinning behavior starts influencing the flow behavior.

- Pressure drop-flow rate profile of aqueous solutions of polyox in low permeability pack (0.12 Darcy) showed three different regions. Initially the profile is linear and the shear thinning behavior starts after certain flow rate. At flow rates higher than a critical value corresponding to critical Deborah number, polyox solutions presented thickening behavior. Thickening behavior was not observed in high permeability pack showing the effect of grain size and permeability on occurrence of dominant elastic effects in porous media.

- Flow performances of 3 wt% aqueous solutions of polyox with different MWD in high permeability (8.9 Darcy) pack were compared. Although the solutions have similar shear viscosity, pressure drop of broad MWD sample was considerably higher than that of narrow MWD. Similar results were also observed in the second group of core flow experiments with low permeability pack (0.12 Darcy) and lower concentration (1 wt %) solutions. This indicates the influence of normal stress (i.e., extensional viscosity effect) and relaxation time (i.e., Deborah number effect) on additional pressure drop during the flow of polymer solutions through porous media.

- The upturn in flow curve (thickening behavior) of polyox solutions with higher relaxation time values occurred at lower shear rates compared to that of solutions with lower values of relaxation time. This reveals the effect of Deborah number on flow behavior of polymer solutions in porous media. Results also indicate that elastic effects on the pressure drop due to the flow of polymer fluids in porous media could be enhanced at constant average molecular weight (without changing shear viscosity) by increasing the MWD of polymer solutions.

- Measured pressure drop due to the flow of weakly elastic polyox solutions in porous media was in relatively good agreement with predictions from Darcy equation. Pressure drop due to the flow of strongly elastic polyox solutions, however, deviated significantly from the pressure drop values predicted by using Darcy equation. It could, therefore, be concluded that high values of normal stress (i.e., extensional viscosity effect) and relaxation time (i.e., Deborah number effect) are the main reasons for the deviation of flow behavior from Darcy law.

- The results of this study indicate that the rheological properties of polymer based fluids used in drilling and well completion operations can be optimized by varying the broadness of the MWD of the polymer. Filtration loss of polymeric drilling fluids could be significantly reduced without increasing shear viscosity of the solution and concentration of the polymer.

7.2 Recommendations:

- The suggested mixing rule predicted more accurate values for average molecular weight and shear viscosity of blended polyox solutions compared to the existing mixing rule in the literature that is based on weighted average molecular weight. The validity of this mixing rule should also be verified using other types of water soluble polymers. This equation should be modified for more accurate predictions of average molecular weight and zero shear viscosity. This could be done by using coefficients for mass fraction of each component of the mixture.

- The influence of MWD on rheological properties of poly ethylene oxide was investigated. However, influence MWD on rheological behavior of polyox blends was not quantified. Polydispersity values (Mw/Mn) of blended samples should be measured by related experimental techniques.

- In order to investigate the influence of extensional viscosity of polyox solutions on pressure drop in porous media, the ratio between normal and shear stress was measured. While, extensional viscosity of polymer solutions should be measured in uniaxial elongational flow.

- It was shown that polymer solutions with broader molecular weight distribution present higher values of normal stress to shear stress ratio, N_1/τ, and relaxation time. More comprehensive investigation of MWD and elastic properties on flow performance of polymer solutions in porous media are required. Polydispersity of polymer blends should be measured by advanced experimental techniques. Extensional viscosity and relaxation time of polymer solutions should be measured by an experimental apparatus with elongational flow configuration.

- Flow experiments were conducted in radial cell packed with glass beads. In order to modify Darcy equation to account for elastic effects, flow experiments should also be conducted in linear cell. It is recommended to use linear cores with high cross sectional area and low length to prevent very high pressure drop values due to the flow of viscoelastic polymer solutions.

References:

Agarwal, P.K., "A Relationship between Steady State Shear Compliance and Molecular Weight Distribution" Macromolecules, 12:342, 1979.

Alfrey, T., Doty, P., "The methods of specifying the properties of viscoelastic material" J. Appl. Phys., 16:700-713, 1945.

Anderssen, R.S., Mead, D.W., "Theoretical derivation of molecular weight scaling for rheological parameters" J Non Newtonian Fluid Mech., 76:299, 1998.

Anna, S.L., McKinley, G.H., "Elasto-Capillary thinning and breakup of model elastic liquids" Journal of Rheology, 45:115-138, 2001.

Bennion, D.R., et al., "Formation damage and horizontal wells-A productivity killer?" SPE 37138, Int. Conf. on Horizontal well Technology, Calgary, 1996.

Bird, R. B., Stewart, W. E., Lightfoot, E. N., "Transport Phenomena", pp. 196-8, Wiley, New York, 1960.

Bird, R. B., Armstrong, R. C., and Hassager, O., Dynamics of Polymeric Liquids, Vol. 1, John Wiley and Sons, New York, 1977.

Bird, R.B., Hassager, O., Armstrong, R.C., Curtiss, C.F., "Dynamics of polymeric Liquids", Vol. 2, Willey: New York, 1977.

Cathey, C.A., Fuller, G.G., "Extensional viscosity measurements of dilute solutions of various polymers" J. Non-Newtonian Fluid Mech., 30:303-316,1988.

Chauveteau, G., Moan, M., Magueur, A., "Thickening Behavior of Dilute Polymer Solutions in Non-Internal Elongation Flows" Journal of Nom-Newtonian Fluid Mechanics, 16:315-327, 1984.

Chauveteau, G., "Rodlike polymer solution flow through fine pores: Influence of pore size on rheological behavior" J. Rheology, 26:111-142, 1982.

Chiappa, L., Menella, A., Lockhart, T. P., Burrafato, G., "Polymer Adsorption at the Brine/Rock Interface: The Pole of Electrostatic and Wettability" Journal of Petroleum Science and Eng., 24:113-122, 1999.

Christopher, R.H., Middleman, S., "Power-Law Flow through a Packed Tube", EC Fundamentals, Vol.4, No. 4., Nov. 1965.

Clasen, C., Fonteios, M.A., Li, J., McKinley, G.H., "The beads-on-string structure of viscoelastic threads" Journal of Fluid Mechanics, submitted.

Clasen, C., Plog, J.P., Kulicke, W.M., Owens, M., Macosko, C.W., Scriven, L.E., Verani, M., McKinley, G.H., "How Dilute are dilute solutions in extensional flows?" J Rheol, 50:849-881, 2006.

Cobianco, S., Bartosek, M., Lezzi, A., Guameri, A., "How to manage Drill-in fluid composition to minimize fluid losses during drilling" SPE/IADC 57581, Middle East drilling technology, conf., Abu Dhabi, UAE, 8-10 November, 1999.

Dauben, D. L., Menzie, D. E., "Flow of Polymer Solutions Through Porous Media" Paper(SPE 1688) was presented at SPE symposium on mechanics of rheologically complex fluids held in Houston, Tex., Dec. 15-16, 1966.

Deiber, J. A., Achowalter E. R., "Modeling the flow of viscoelastic fluids through porous media" AIChE Journal 27:912, 1981.

Denn, M. M., Marrucci, G., "Stretching of viscoelastic liquids" AIChE Journal, 17:101, 1971.

Doi, M., Edwards, S.F., "The theory of polymer dynamics" Oxford: Clarendon Press, 1986.

Durst, F., Haas, R., Interthal, W., "The Nature of Flows through Porous Media" J. of Non-Newtonian Fluid Mechanics, 22:169-189, 1987.

Entov, V.M., Hinch. E.J., "Effect of a Spectrum of Relaxation times on the capillary thinning of a filament of Elastic Liquid" J. Non-Newtonian Fluid Mech., 72:31-54, 1997.

Ferry, J.D., "Viscoelastic properties of polymers" 3rd ed. New York: Wiely, 1980.

Garrocuh, A. A., Gharbi, R. B., "A Novel Model for Viscoelastic Fluid Flow in Porous Media" paper SPE 102015, 2006 SPE Annual Technical Conference and Exhibition held in San Antonio, Texas, U.S.A., 24-27 September 2006.

Ghoniem, S.A., "Extensional flow of polymer solutions through porous media" Rheol Acta, 24:588, 1985.

Graessley, W.W., "The entanglement concept in polymer rheology" Adv. Polym Sci; 16:1, 1974.

Gupta, R. K., Sridhar, T., "Viscoelastic effects in non-Newtonian flows through porous media" Rheol. Acta 24:148-151,1985.

James, D.F., McLaren, D.R., "The laminar flow of dilute polymer solutions through porous media" J Fluid Mechanics, 70:733, 1975.

Jenni, L. Briggs, "Haake CaBER® 1 Theory & Application"

Jones, D.M., Walters, K., "The behavior of polymer solutions in extension-dominated flows, with application to Enhanced Oil Recovery" Rheol Acta 28:482-498,1989.

Jones, K., "The Rheology of Viscoelastic Fluids for Oil Recovery: A Study of Micellar/Polymer Flow over a Wide Range of Shear Rates in porous Media." M.S. Thesis, the University of Texas at Austin, Austin, TX, 1981.

Jones, D.M., Walters, K., Williams, P.R., "On the extensional viscosity of mobile polymer solutions" Rheol Acta, 26:20, 1987.

Kemblowski, Z., Dziubinski, M., "Resistance to flow of molten polymers through granular beds" Rheol Acta 17:176, 1978.

Khan, R., Kuru, E., "A Study of the Mechanisms of Internal Cake Formation During Drilling, Well Completion and Hydraulic Fracturing Operations", presented at Annual Technical Conference, Islamabad, 8-9 October.

Kulicke, W.M., Fließverhaltenvon Stoffen und Stoffgemischen. Huthig und Wepf, Basel, Heidelberg, New York, 1986.

Leonardi, F., Allal, A., and Marin, G., "Molecular weight distribution from viscoelastic data: The importance of tube renewal and Rouse modes" J. Rheol., 46:202-224, 2002.

Li, W., Dobraszczyk, B.J., Schofield, J.D., "Stress relaxation behavior of wheat dough, gluten, and gluten propein fractions" Cereal Chem. 80(3):333-338, 2003.

Liu, Y.M., Shaw, M.T., Tuminello, W.H., "Obtaining molecular weight distribution information from the viscosity data of linear polymer melts" Journal of Rheology, 42:453-476, 1998.

Lucy, E. Rodd, Timothy, P. Scott, Justin, J. Cooper-White, Gareth, H. Mckinley, "Capillary Break-up Rheometry of Low-Viscosity Elastic Fluids" Appl. Rheol. 15: 12-27, 2005.

Marshal, R. J., Metzner, A. B., "Flow of Viscoelastic Fluids Through Porous Media" paper SPE 1687 presented at the Society of Petroleum Engineers Symposium on Mechanics of Rheologically Complex Fluids, Houston, Tex., Dec. 15-16, 1966.

Massarani, G., Fluidodinamica em Sistemas Particulados, (In Portuguese) Editora UFRJ, Rio de Janeiro, Brazil, 1997.

Malkin, AYa, Blinova N.K., Vinogradov, G.V., Zabugina, M.P., Sabsai, OYu, Shalganova, V.C., Kirchevskaya, IYu, Shatalov, V.P., "On rheological properties of polydisperse polymers" Eur Polym J, 10:445, 1974.

Martins, A. L., "Quantificacao das Forcas Resistivas no Escoamento de Solucoes Polimericas em Meios Porosos e Seu Impacto na Engenharia de pocos de Petroleo", MSc Dissertation (In Portuguese), COPPE/Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brazil, 2004.

Marshall, R., Metzner, A.B., "Flow of Viscoelastic Fluids through Porous Media" IEC Fund., 6:393, 1967.

Martins, A.L., Waldmann, A.T.A., Riberio, D.C., Massarani, G. "The Conceptual Design of a Nom-Invasive Solids Free Drill-in Fluid" SPE 94287, Madrid, Spain, 13-16 June 2005.

Massarani, G., Silva Telles, A., "An Extended Capillary Model for Flows in Porous Media" Journal of Porous Media, Vol. 4, n.4, p.297-307, 2001.

McGrory, W. J., Tuminello, W. H., "Determine the molecular weight distribution from stress relaxation properties of a melt" J. Rheol., 34:867-890, 1990.

McKelvey, J. M., "Polymer Processing", p. 69, Wiley, New York, 1962.

McKinley, G.H., Tripathi, A., "How to Extract the Newtonian viscosity from capillary Breakup measurements in a Filament Rheometer" J. Rheol., 44:653-671, 2000.

Merril, E. W., "Non-Newtonian in thin liquids; Molecullar and Physical Aspects", Modern Chemical Engineering, Reinhold Publishing Corp., New York, 1963.

Mills, J., "The rheological properties and molecular weight distribution of polydimethylsiloxane" Eur Polym J, 5:675, 1969.

Mohsen Safari-Ardi, Nhan Phan-Thien, "Stress Relaxation and Oscillatory tests to distinguish between doughs prepared from wheat flours of different variental origin" Cereal Chem. 75(1):80-84 (1998).

Montfort, J.P., Marin, G., Arman. J., Monge, P.h., "Blending law for binary blends of fractions of linear polystyrene" Polymers, 19:277, 1978.

Navarete, R.C., Himes, R.E. and Seheult, J.M.: "Applications of Xanthan Gum in Fluid-Loss Vontrol and Related Formation Damage", paper SPE 59535, SPE Permiam Basin Oil and Gas recovery Conference, Midland, Texas, March, 21-23, 2000.

Navarrete, R.C., Mitchelll, J.P., "Fluid-Loss control for high-permeability rocks in hydraulic fracturing under realistic shear conditions" SPE 29504, SPE production operations symposium, Oklahoma city, U.S.A, 2-4 April, 1995.

Parlar, M., Nelson, E.B., Walton, I.C., Park, E., Debonis, V., "An experimental study on fluid loss behavior of fracturing fluids and formation damage in high permeability porous media" SPE 30458. SPE ATCE, Dallas, U.S.A., 22-25, October 1995.

Penny, G.S., Conway, M.W., "Fluid Leak-off" resent advances in hydraulic fracturing" SPE Monograph, Vol.12, Richardson, TX, pp.147-176, 1989.

Plog, J.P., Kulicke, W.M., Clasen, C., "Influence of the Molar Mass Distribution on the Elongational Behavior of Polymer Solutions in Capillary Break up" Appl. Rheol., 15:28-37, 2005.

Ressia, J.A., Aillar, M.A., Valles, E.M., "Influence of polydispersity on the viscoelastic properties of linear polydimethylsiloxanes and their binary blends" Polymer 41:6885-6894, 2000.

Saasen, H., "Influence of linear viscoelastic properties on invasion of drilling fluid filtrate into a porous formation" Oil Gas-European Magazine, 4, 1990.

Sadowski, T.J., Bird, R.B., "Non-Newtonian Flow through Porous Media. I. Theoretical", Transaction of the Society of Rheology" 9:2, 243-250, 1965.

Sadowski, "Non-Newtonian Flow through Porous Media. II. Experimental", Transaction of the Society of Rheology, 9:2, 251-271,1965.

Savins, J.G., "Non-Newtonian Flow through Porous Media" Industrial and Engineering Chemistry, 61(10):18,1969.

Shaw, M.T., Tuminello, W.H., "A Closer Look at the MWD-Viscosity Transform" Polymer Engineering and Science, 34:159-165, 1994.

Song L.Ng., Robert P.Mun, David V. Boger, David, F. James, "Extensional viscosity measurements of dilute solutions of various polymers" J. Non-Newtonian Fluid Mech., 65:291-298, 1996.

Stelter M. et al., "Investigation of the elongational behavior of polymer solutions by means of an elongational rheometer", Journal of Rheology 46:507-527, 2002.

Struglinski, M.J., Graessley, W.W., "Effects of polydispersity on the linear viscoelastic properties of entangled polymers. 1. Experimental observations for binary mixtures of linear polybutadiene" Macromolecules, 18:2630, 1985.

Svendsen, O., Saasen, A., Vassoy, Skogen, E., Mackin, F., Normann, S.H., "Optimum Fluid Design for Drilling and Cementing a Well Drilled with Coil Tubing Technoology" SPE 50405, SPE International Conference on Horizontal Well Technology, Calgary, Canada, 1-4, November, 1998.

Teeuw, D., Hesselink, F., "Power-Law Flow and Hydrodynamic Behavior of Biopolymer Solutions in Porous Media" Soc. Petr. Eng. Int. Symp. On Oilfield and Chemistry, SPE 8982, Stanford, CA, May 28-30, 1980.

Van Poollen, H. K., Jargon, J. R., "Steady state and unsteady state flow of non-Newtonian fluids through porous media" In AIME Transactions: Dallas, TX, 1969, Vol. 246, p 80.

Willhite, G.P., Uhl, J. T., "Correlation of the mobility of biopolymer with polymer concentration and rock properties in sandstone" Polymeric Science and Engineering, 55:577, 1986.

Wissler, E. H., "Viscoelastic Effects in the Flow of Non-Newtonian Fluids through a Porous Medium" Ind. Eng. Chem. Fundam., 10:411, 1971.

Walters, K., Rheometry. Chapman and Hall: London, 1975.

Wasserman, S. H., "Calculating the molecular weight distribution from linear viscoelastic response of polymer melts" J. Rheol., 39:601-625, 1995.

Wreath, D., Pope, G., Sepehrnoori, K., "Dependence of Polymer Apparent Viscosity on the Permeable Media and Flow Conditions" In Situ., 14:263, 1990.

Yuan, M., "A Rheological Study of Polymer and Microemulsion in Porous Media" M.S. Thesis, The University of Texas at Austin, Austin, TX, 1981.

Zang, Y.H., Muller, R., Froelich, D., "Influence of molecular weight distribution of viscoelastic constants of polymer melts in the terminal zone. New blending law and comparison with experimental data" Polymer 28:1577, 1987.